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FINAL REPORT

RADIATION POLYMERIZATION
OF
ACETYLENE DERIVATIVES

10 August 1961 - 10 August 1962

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MONSANTO RESEARCH CORPORATION
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Monsanto BOSTON
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RADIATION POLYMERIZATION OF ACETYLENE DERIVATIVES

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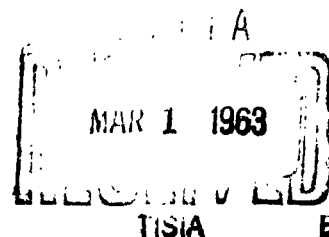Contract No. NObs-86072

OBJECT

Investigate the radiation induced
polymerization of acetylene
derivatives as a means of preparing
high polymers that are thermally
stable and useful as semiconductors.

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I. SUMMARY

Exploratory research on the radiation-induced polymerization of acetylene derivatives to produce polyene polymers with useful properties included synthesis of acetylene derivatives, screening monomers for radiation sensitivity, correlation of chemical structure with sensitivity, attempts to establish optimum polymerization conditions, and characterization of the products.

Fifteen acetylene derivatives representing seven compound classes were prepared, and five others were supplied by the Research and Engineering Division of Monsanto Chemical Company. Eight other syntheses were attempted unsuccessfully. A total of 48 acetylene derivatives were screened for radiation sensitivity during the year. Radiation yields with G values* greater than 100 were observed with propiolic acid, G = 322; 2-butyn-1,4-dipropiolate, G = 103; neopentylene dipropiolate, G = 177; and pentaerythritol tetrapropiolate, G = 113. Other moderately radiation sensitive systems include: phenylpropiolic acid, G = 73; phenylbromoacetylene, G = 94; 2-butyn-1,4-diacetate, G = 96 and bis-1,4-(hydroxyethyloxy)-butyne-2, G = 57. In general, the acetylenic monomers exhibit good radiation sensitivity, but the products obtained appear to be of low molecular weight.

Based on the screening data, radiation sensitivity was correlated with chemical structure. Among the functional groups affecting radiation sensitivity, the carboxyl group appeared especially sensitive. Presence of the hydroxyl group appeared unrelated to radiation sensitivity. Whereas monopropiolates were only fairly radiation-sensitive, all polypropiolate esters studied were very radiation sensitive.

In attempts to define optimum conditions for radiation-induced polymerization by use of radiation-sensitive acetylene derivative models, the following variables were studied: state; dose rate; temperature; and use of complexing agents and sensitizers. All affected the radiation yields, but no consistent pattern emerged.

The products obtained from the above studies were mostly highly colored fluids, indicating low molecular weights. The few solids obtained were evaluated for electrical properties and resistivity values ranging from 1.6×10^5 to 10^{13} ohm-cm were obtained. However, the polymers differed little in electrical properties from the corresponding monomers.

*G value = number of monomer molecules that polymerize per 100 ev of radiation.

II. PURPOSE

This investigation concerns the radiation-induced polymerization of acetylene derivatives as a means of preparing high polymers that are thermally stable and potentially useful as semiconductors. Fulfilling this major objective includes establishing optimum radiation conditions for polymerization or copolymerization to high molecular weight materials, and evaluation of the products for their mechanical, physical, thermal, hydrolytic, and semiconductor properties. The ultimate objective was to develop polymeric materials that are useful in low-level nuclear radiation detectors, infrared detectors, and solar photovoltaic converters at temperatures 'higher than the limiting temperature for present silicon devices.

Secondary objectives included correlation of chemical structure with radiation sensitivity and an increased understanding of the mechanism of radiation-induced chemical reactions.

III. DISCUSSION

A. BACKGROUND   The radiation-induced polymerization of acetylene derivatives was undertaken as a means of producing polyene polymers that might have unique and useful properties. In general, long chain polymers with uninterrupted conjugation are expected to be thermally stable and to have semiconducting properties which could lead to practical applications.

The development of radiation produced polymers suitable for semiconductor devices such as nuclear radiation detectors, IR detectors and solar photovoltaic converters, requires the following steps: (1) radiolytic preparation of suitable polymers; (2) physical and electrical testing; and (3) selection of those materials potentially applicable in specific devices.

In the first phase polyenes were selected as a class that could have semiconductor properties and that could be obtained via the radiation-induced polymerization of acetylene derivatives. Such polyenes should have a relatively high molecular weight and high melting point. In addition, they should be obtainable in quantities adequate for electrical tests. These criteria are quite formidable and have consequently required most of the effort in this study.

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It must be emphasized that the preparation of suitable polyenes must be solved before the more practical testing and evaluation phases can be undertaken. Their preparation included: (1) screening studies to find acetylene derivatives sensitive to radiation induced polymerization; (2) synthesis of specific acetylene derivatives; (3) correlation of radiolytic sensitivity with chemical structure; and (4) definition of optimum polymerization conditions to produce polyenes suitable for semiconductor tests. Work accomplished during this year included each of these areas in addition to limited chemical, physical and electrical tests on specific polymers.

B. **ACETYLENIC DERIVATIVE PREPARATION**   Fifteen acetylenic materials representing seven compound classes were synthesized for radiolytic testing. Included were seven propiolate esters, prepared by p-toluenesulfonic acid catalyzed esterification: methyl propiolate, (36%); n-butyl propiolate, (73%); isobutyl propiolate, (56%); sec-butyl propiolate, (30%); propargyl propiolate, (28%); neopentylene dipropiolate, (89%); and 2-butyn-1,4-dipropiolate.

Methyl propiolate was screened as the simplest propiolate ester and used for study of the effect of acetylene bond complexes such as the known methyl propiolate/pyridine complex on radiation-induced polymerization. Irradiation of complexed triple bonds may facilitate polymerization to long chain polyenes, especially if the resulting polyene is complexed or is protected from further interaction.

Isomeric butyl propiolates were prepared to correlate chemical structure with radiation sensitivity. Propargyl propiolate was screened as a model having an acetylenic group in both the acyl and alkyl portions of the ester.

Neopentylene dipropiolate was prepared on a 2/3 mole scale to allow sufficient material for study of the effect of temperature and state on radiation polymerization.

The butyne dipropiolate was selected as an analog of neopentylene dipropiolate which readily forms solid polymers with radiation. Neopentylene dipropiolate polymers are highly crosslinked via the fully saturated neopentylene group which inhibit charge transfer between the chains. Thus replacement of the neopentylene group with the electron-rich linear butynylene group could lead to easier charge transfer and higher conductivity.

Phenylbromoacetylene was prepared in 11% yield by the interaction of sodium hypobromite with phenylacetylene, and phenyliodoacetylene was prepared in 65% yield by the direct iodination of phenylacetylene in liquid ammonia. These models of a disubstituted acetylene contain a radiation-sensitive carbon-halogen bond and should polymerize to a polyene containing no hydrogens on the carbon chain.

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A third disubstituted acetylene model was diiodoacetylene, made in a 68% yield by the direct iodination of acetylene in liquid ammonia. This hazardous monomer, which explodes with friction or shock, should yield a polyene containing only carbon and iodine.

Two other acid derivatives were prepared for radiolytic screening. Acetylene dicarboxamide was prepared in 78% yield, by conventional ammonolysis of the corresponding methyl ester. Propiolyl chloride was synthesized in 18% yield by reaction of propiolic acid with benzoyl chloride.

Phenylpropiolic acid and phenylpropargyl aldehyde were made to extend the phenylacetylene series for study of the effect of substituents on radiolytic polymerization. Phenylpropiolic acid was made in a 2-step reaction starting with ethyl cinnamate. Bromination to ethyl α,β-dibromo-β-phenylpropionate (82% yield) and subsequent dehydrobromination and hydrolysis in ethanolic potassium hydroxide gave phenylpropiolic acid (47% yield). Propiolic acid polymerizes under irradiation in good yield to low molecular weight materials. The phenylpropiolic acid was screened to see if substitution of the acetylenic hydrogen increases the degree of polymerization (by reduction of the chain transfer process).

Phenylpropargyl aldehyde was made in a 4-step synthesis beginning with cinnamaldehyde. Bromination of the aldehyde (66% yield), protection of the aldehyde group of the bromo compound by conversion to the acetal (83% yield), and dehydrobromination of the acetal (90% yield) gave phenylpropargyl aldehyde acetal. Decomposition of the acetal to phenylpropargyl aldehyde gave poor yields (6%) due to thermal polymerization of the desired product during distillation.

C. SCREENING STUDIES   Screening studies were conducted to define the radiation sensitivity of the acetylenic bond and the scope of such sensitivity. Results are encouraging.

Forty-eight acetylene derivatives were radiolyzed with Co-60 gamma-rays at dosages of 14 to 64 megareps (dose rate of 0.7 megarep/hr) to measure their radiation sensitivity. Monomers used are summarized in Tables I and II and the radiation conditions and results in Table III.

Most radiolyses were conducted with purified materials in pyrex break-seal tubes under vacuum. The tubes were loaded via a specially built vacuum line (Figure 1) and placed in a five-tube sample holder (Figure 5) for radiolysis with a 590 curie Co-60 source (Figures 6, 7, 8, 9, and 10). These radiolyses were

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performed by placing the sealed Co-60 rod into the sample holder center tube (Figure 5) which was surrounded by the five tubes containing the glass sample tubes. Dosimetry measurements showed a dose rate of 7×10^5 rep/hr and demonstrated that equal intensities were delivered to each tube.

The acetylenic compounds used were synthesized or selected from those available either commercially or as research samples in Monsanto. The sources of specific compounds are listed in Table II along with the purification method. Most of the solid compounds were irradiated at ambient temperatures. Liquid samples were screened at dry ice temperatures.

After irradiation, the break-seal sample tubes were opened into the vacuum line. No significant gaseous products were observed. Where possible, the starting material was distilled from the sample tube, and the residue was weighed. This residue, called "polymer" in this report, included all materials boiling higher than the starting compound. The polymer yield is expressed in Table III as weight percent and as G value, the radiation yield. This latter value is the number of monomer molecules that react to form polymer per 100 ev of radiation.

$$G \text{ (polymer)} = \frac{N \times \text{moles of monomer going to polymer/gm}}{I \times C}$$

where N = Avogadro's number
I = dose in rep
C = conversion factor for rep to 100 ev/gm

Table III summarizes the polymer yields and visual and physical property changes effected by radiation. The polymer yields of 1 to 84% and radiation yields of 4 to 322 are encouraging. The relationship between chemical and radiolytic yield is not linear since the latter depends on molecular weight and radiation dose. In general, radiation yields above 3 are assumed to indicate chain reactions since an average of ~33 ev is required for the formation of a radical or an ion pair. Thus, the radiation yields obtained indicate chain processes.

In most cases, however, the polymers obtained were heavy syrups, indicating relatively low molecular weight.

The most radiation-sensitive system uncovered was propiolic acid (G≥200). However, the product was of low molecular weight since less than 10% was non-distillable under high vacuum. Other highly sensitive systems observed were as follows: among the alcohols and diols, 1-ethynylcyclohexanol (G = 32) and butyndiol (G = 40) were the most sensitive. Among the acids, in addition to propiolic acid, phenylpropiolic acid (G = 73) was also very sensitive and gave a solid polymer.

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TABLE I

STRUCTURAL FORMULAS OF ACETYLENIC DERIVATIVES STUDIED

Name	Formula

Alcohols

1-Butyn-3-ol	$HC \equiv C-CH(OH)CH_3$
3,5-Dimethyl-1-hexyn-3-ol	$HC \equiv C-C(OH)(CH_3)CH_2CH(CH_3)_2$
1-Ethynylcyclohexanol	$HC \equiv C-C-OH$
	$\quad CH_2 \quad CH_2$
	$\quad CH_2 \quad CH_2$
	$\quad \quad CH_2$
3-Methyl-1-butyn-3-ol	$HC \equiv C-C(OH)(CH_3)_2$
3-Methyl-1-pentyn-3-ol	$HC \equiv C-C(OH)(CH_3)CH_2CH_3$
Propargyl alcohol (1-propyn-3-ol)	$HC \equiv C-CH_2OH$

Diols

2-Butyn-1,4-diol	$CH_2OH-C \equiv C-CH_2OH$
2,5-Dimethyl-3-hexyn-2,5-diol	$C(CH_3)_2OH-C \equiv C-C(OH)(CH_3)_2$
3,6-Dimethyl-4-octyn-3,6-diol	$C(CH_3)(C_2H_5)OH-C \equiv C-C(OH)(CH_3)(C_2H_5)$
2,5-Diphenyl-3-hexyn-2,5-diol	$C(CH_3)OH-C \equiv C-C(OH)(CH_3)$

Acids

Acetylenedicarboxylic acid	$HOOC-C \equiv C-COOH$
Phenylpropiolic acid	$C \equiv C-COOH$ (phenyl)
Propiolic acid	$HC \equiv C-COOH$

Esters

n-Butyl propiolate	$HC \equiv C-COO(CH_2)_3CH_3$
sec-Butyl propiolate	$HC \equiv C-COOCH(CH_3)CH_2CH_3$
iso-Butyl propiolate	$HC \equiv C-COOCH_2CH(CH_3)_2$
t-Butyl propiolate	$HC \equiv C-COOC(CH_3)_3$
2-Butyn-1,4-dipropiolate	$HC \equiv C-COOCH_2C \equiv C-CH_2OCO-C \equiv CH$
p-Carboethoxyphenyl propiolate	$HC \equiv C-COO- \langle \rangle -COOC_2H_5$
Dimethyl acetylenedicarboxylate	$CH_3-OCO-C \equiv C-COOCH_3$
Ethyl propiolate	$HC \equiv C-COOCH_2CH_3$
Methyl propiolate	$HC \equiv C-COOCH_3$
β-Naphthyl propiolate	$HC \equiv C-COO-$ (naphthyl)

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TABLE I (Cont'd.)

Name	Formula
Neopentylene dipropiolate	$(HC\equiv C\text{-}COOCH_2)_2C(CH_3)_2$
Pentaerythritol tetrapropiolate	$(HC\equiv C\text{-}COOCH_2)_4C$
Propargyl propiolate	$HC\equiv C\text{-}COOCH_2\text{-}C\equiv CH$

Acid Derivatives

Acetylenedicarboxamide	$NH_2CO\text{-}C\equiv C\text{-}CONH_2$
Acetylenedicarboxylic acid, mono-potassium salt	$HOCO\text{-}C\equiv C\text{-}COOK$
N-(p-Carboethoxyphenyl)propiolamide	$HC\equiv C\text{-}CONH\text{-}\langle\bigcirc\rangle\text{-}COOC_2H_5$
Propiolyl chloride	$HC\equiv C\text{-}COCl$

Halides

5-Chloro-1-pentyne	$HC\equiv C(CH_2)_3Cl$
1,4-Dichloro-2-butyne	$ClCH_2\text{-}C\equiv C\text{-}CH_2Cl$
Diiodoacetylene	$IC\equiv CI$
Phenylbromoacetylene	$\langle\bigcirc\rangle\text{-}C\equiv C\text{-}Br$
Phenyliodoacetylene	$\langle\bigcirc\rangle\text{-}C\equiv C\text{-}I$
Propargyl bromide (3-bromo-1-propyne)	$HC\equiv C\text{-}CH_2Br$
Propargyl chloride (3-chloro-1-propyne)	$HC\equiv C\text{-}CH_2Cl$

Hydrocarbons

Diphenylacetylene	$C_6H_5C\equiv C\text{-}C_6H_5$
1-Dodecyne	$HC\equiv C\text{-}(CH_2)_9CH_3$
3-Methyl-3-buten-1-yne	$HC\equiv C\text{-}C(CH_3)=CH_2$
Phenylacetylene (ethynylbenzene)	$HC\equiv C\text{-}C_6H_5$

Miscellaneous

Bis-1,4-(hydroxyethyloxy)butyne-2	$HO(CH_2)_2\text{-}O\text{-}CH_2\text{-}C\equiv C\text{-}CH_2\text{-}O\text{-}(CH_2)_2OH$
2-Butyn-1,4-diacetate	$CH_3COOCH_2\text{-}C\equiv C\text{-}CH_2\text{-}OCO\text{-}CH_3$
Diethylpropargylamine	$HC\equiv C\text{-}CH_2\text{-}N(C_2H_5)_2$
Ethoxyacetylene	$HC\equiv C\text{-}O\text{-}C_2H_5$
Phenylpropargyl aldehyde	$C_6H_5C\equiv C\text{-}CHO$
Phenylpropargyl aldehyde acetal	$C_6H_5C\equiv C\text{-}CH(OC_2H_5)_2$

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TABLE II

ACETYLENE DERIVATIVES USED IN
RADIATION POLYMERIZATION

System	Source	Purification
Alcohols		
1-Butyn-3-ol	Farchan	Distill
3,5-Dimethyl-1-hexyn-3-ol	Air Reduction Chem.	Distill
1-Ethynylcyclohexanol	Air Reduction Chem.	Distill
3-Methyl-1-butyn-3-ol	Air Reduction Chem.	Distill
3-Methyl-1-pentyn-3-ol	Air Reduction Chem.	Distill
Propargyl alcohol	Matheson Coleman & Bell	Distill
Diols		
2-Butyn-1,4-diol	General Aniline & Film	Distill
2,5-Dimethyl-3-hexyn-2,5-diol	Air Reduction Chem.	None
3,6-Dimethyl-4-octyn-3,6-diol	Air Reduction Chem.	None
2,5-Diphenyl-3-hexyn-2,5-diol	Air Reduction Chem.	Distill
Acids		
Acetylenedicarboxylic acid	Aldrich Chem.	None
Acetylene dicarboxylic acid, anhyd.	Aldrich Chem.	Dried over H_2SO_4
Phenylpropiolic acid	Synthesized	Distill
Propiolic acid	Aldrich Chem.	Distill
Esters		
n-Butyl propiolate	Synthesized	Distill
sec-Butyl propiolate	Synthesized	Distill
iso-Butyl propiolate	Synthesized	Distill
2-Butyn-1,4-dipropiolate	Synthesized	Distill
p-Carboethoxyphenyl propiolate	Monsanto, R&E	None
Dimethyl acetylenedicarboxylate	Matheson Coleman & Bell	Distill

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TABLE II (Cont'd.)

System	Source	Purification
Ethyl propiolate	Farchan	Distill
Methyl propiolate	Synthesized	Distill
β-Naphthyl propiolate	Monsanto, R&E	None
Neopentylene dipropiolate	Monsanto, R&E synthesized	Distill recrystallized
Pentaerythritol tetrapropiolate	Monsanto, R&E	None
Propargyl propiolate	Synthesized	Distill

Acid Derivatives

Acetylenedicarboxamide	Synthesized	Dried over H_2SO_4
Acetylenedicarboxylic acid, monopotassium salt	Aldrich Chem.	None
Acetylenedicarboxylic acid, monopotassium salt, anhyd.	Aldrich Chem.	Dried over H_2SO_4
N-(p-Carboethoxyphenyl)propiol-amide	Monsanto, R&E	None
Propiolyl chloride	Synthesized	Distill

Halides

5-Chloro-1-pentyne	Farchan	Distill
1,4-Dichloro-2-butyne	General Aniline & Film	Distill
Diiodoacetylene	Synthesized	Distill
Phenylbromoacetylene	Synthesized	Distill
Phenyliodoacetylene	Synthesized	Distill
Propargyl bromide	Matheson Coleman & Bell	Distill
Propargyl chloride	Aldrich Chem.	Distill

Hydrocarbons

Diphenylacetylene	Matheson Coleman & Bell	None
1-Dodecyne	Farchan	Distill
3-Methyl-3-buten-1-yne	Matheson Coleman & Bell	Distill
Phenylacetylene	Matheson Coleman & Bell	Distill

TABLE II (Cont'd.)

System	Source	Purification
Miscellaneous		
Bis-1,4-(hydroxyethyloxy)butyne-2	General Aniline & Film	Distill
2-Butyn-1,4-diacetate	General Aniline & Film	Distill
Diethylpropargylamide	Peninsular Chem.	Distill
Ethoxyacetylene	Pfister Chem.	Distill
Phenylpropargyl aldehyde	Synthesized	Distill
Phenylpropargyl aldehyde acetal	Synthesized	Distill

TABLE III

RESULTS FROM RADIATION-INDUCED POLYMERIZATION OF ACETYLENIC DERIVATIVES

Run	System	Time, hr.	Temp., °C Low	Temp., °C Hi	Dose, megarep	Polymer % Yield	Polymer G⊕ Value	Remarks
Alcohols								
1905	1-Butyn-3-ol	43	-78	-36	30	2	9	
240	3,5-Dimethyl-1-hexyn-3-ol	40	-78	-36	28	6	18	
3448	1-Ethynylcyclohexanol	39	-74	-36	27	9	32	
241	3-Methyl-1-butyn-3-ol	40	-78	-30	28	5	20	
4902	3-Methyl-1-pentyn-3-ol	42	-76	-39	30	5	20	
218	Propargyl alcohol	42	-74	-30	29	2	14	
Diols								
219	2-Butyn-1,4-diol	42	-74	-30	29	9	40	
3440	2,5-Dimethyl-3-hexyn-2,5-diol	66	22	30	46	3	6	
3441	3,6-Dimethyl-4-octyn-3,6-diol	66	22	30	46	3	4	
243	2,5-Diphenyl-3-hexyn-2,5-diol	68	5	24	48	11	10	
Acids								
213	Acetylenedicarboxylic acid	20	20	28	14			
216	"	65	23	32	46			
237	"	72*	22	28	51			
247	"		Exploded during run					
1909	Acetylenedicarboxylic acid, anhydrous	67	20	24	48			
225	"	40	-78	-30	28			
236	"	72*	22	28	51			
249	"		Exploded during run					
1919	"	67	10	19	47			
3420	"		Exploded during run					
3444	Phenylpropiolic acid	66	5	8	47	43	73	Corrected for 7% thermal polymer
232	Propiolic acid	40	-75	-38	28	35	204	
1911	"	40	-75	-34	28	55	322	
1916	"	40	-74	-30	28	32	184	
4926	"	41	-78	-40	29	24	136	
4936	"	21	-75	-37	15**	3	31	
3432	"	0.01	-75		37**	6	25	
4950	"	0.02	-75		74**	12	27	
7360	"	162	14		115	34	49	
4927	"	41	19	39	29	13	73	
4933	Propiolic acid/t-butanol (49/51)	41	99	101	29	14	73	G(-butanol) = 36
1921	" /water (50/50)	40	-74	-27	28	11	148	G(-water) = 182
3423	" /acetonitrile (65/35)	40	-78	-37	30	51	76	G(-acetonitrile) = 72
4946	" /phenylacetylene (34/66)	42	-78	-30	30	21	37	G(-phenylacetylene) = 50
7351	" /diphenylacetylene (30/70)	42	-78	-30	30	20	1	G(-diphenylacetylene) = 18
1914	" /sec-butyl propiolate (65/35)	40	-74	-30	28	9	194	G(-sec-butylpropiolate) = 40
7364	" /benzoquinone (99/1)	40	15	39	29	46	91	
7366	" /ethyl ether (49/51)	40	15	39	29	16	36	G(-ethyl ether) = 12
7352	" /maleic anhydride (42/58)	75	22	33	53	14	44	G(-maleic anhydride) = 52
4939	" /low-pressure polyethylene (90/10)	41	26	35	29	38	48	
4944	" /polyacrylonitrile (90/10)	41	26	35	29	8	98	
7368	" /diiodoacetylene (43/57)	88	75	80	63	17	6	G(-diiodoacetylene) = 38; not corrected for thermal polymer
7362	" /phenylacetylene (41/59)	65	120	120	46	56	102	G(-phenylacetylene) = 69; not corrected for thermal polymer

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TABLE III (Cont'd.)

RESULTS FROM RADIATION-INDUCED POLYMERIZATION OF ACETYLENIC DERIVATIVES

Run	System	Irradiation Conditions			Polymer		Remarks
		Time, hr.	Temp., °C Low / Hi	Dose, megarep	% Yield	G⊕ Value	
Esters							
3409	n-Butyl propiolate	41	-79 / -36	29	0.9	20	
3414	sec-Butyl propiolate	41	-79 / -36	29	8	25	
3417	iso-Butyl propiolate	41	-75 / -35	29	5	17	
4905	2-Butyn-1,4-diproplolate	42	-76 / -39	30	51	103	
244	p-Carboethoxyphenyl propiolate	88	22 / 27	62	36	30	
223	Dimethyl acetylenedicarboxylate	40	-78 / -30	28	15	43	
1906	Ethyl propiolate	40	-75 / -32	28	9	39	
3442	Methyl propiolate/pyridine (52/48)	39	-74 / -36	27	5	14	Values corrected for 17.3% solids formed in absence of rad
3443	" " (31/69)	39	-74 / -36	27	10	10	Values corrected for 19.2% solids formed in absence of rad
4901	Methyl propiolate	42	-76 / -30	30	4	20	
245	β-Naphthyl propiolate	88	22 / 27	62	34	37	
3424	"	67	80 / 80	47	15	18	
242	Neopentylene diproplolate	68	5 / 24	48	84	97	
1910	"	68	20 / 26	48	46	54	
1923	"	67	21 / 26	48	37	43	
1930	"	42	65 / 65	30	95	177	
1941	"	42	-77 / -36	30	54	101	
1947	"	46	150 / 150	33	99	167	
3403	"	47	150 / 150	33	100	165	
3404	"	47	65 / 65	33	54	91	
3415	"	41	-79 / -36	29	33	63	
3430	"	0.01	-75 / -36	37**	46	68	Includes post-irradiation effect
1928	Pentaerythritol tetrapropiolate	42	-20 / 28	30	100	113	Product - infusible solid
3410	Propargyl propiolate	41	-79 / -36	29	12	43	Irradiated as pellet
Acid Derivatives							
3413	Acetylenedicarboxamide	42	8 / 17	30			
210	Acetylenedicarboxylic acid, monopotassium salt	20	24 / 34	14			
212	"	20	-74 / -23	14			
235	"	72*	22 / 28		Exploded during run		
248	"	72*	22 / 28	51			
234	" , anhydrous			51			
250	"				Exploded during run		
1903	"	12	100 / 175	8			Product is infusible solid
1918	"	67	10 / 19	47			
246	N-(p-Carboethoxyphenyl)propiolamide	88	22 / 27	62	61	52	
4910	Propiolyl chloride	42	-75 / -34	30	6	25	
Halides							
3428	5-Chloro-1-pentyne	42	-75 / -27	30	5	18	
4924	1,4-Dichloro-2-butyne	43	-75 / -32	30	4	13	
3418	Diiodoacetylene	42	8 / 17	30	18	26	
4909	"	96	14 / 24	68	11	7	
4913	Diiodoacetylene/2,2-dimethylbutane (81/19)	48	12 / 19	34	1	2	
4925	"	68	14 / 19	48	14	9	
1933	Phenylbromoacetylene	42	-77 / -36	30	45	94	
4934	Phenyliodoacetylene	41	-78 / -34	29	3	4	
220	Propargyl bromide	40	-76 / -38	28	9	30	
221	"	40	-76 / -38	28	0	34	
1912	Propargyl chloride	40	-75 / -34	28	3	18	

TABLE III (Cont'd.)

RESULTS FROM RADIATION-INDUCED POLYMERIZATION OF ACETYLENIC DERIVATIVES

Run	System	Irradiation Conditions				Polymer		Remarks
		Time, hr.	Temp., °C Low	Hi	Dose, megarep	% Yield	G ⊕ Value	
Hydrocarbons								
4947	Diphenylacetylene	0.03			112**	18	10	
214	"	20	20	28	14	1	4	Final 75 hr at 120°C
7363	"	238	14	120	168	1	0.5	
4941	"	42	120	120	30	1	3	
239	1-Dodecyne	40	-78	-30	28	16	38	
1931	3-Methyl-3-buten-1-yne	42	-77	-36	30	2	10	
224	"	40	-78	-30	28	3	11	
7355	Phenylacetylene	0.05	-70		186**	6	4	
4949	"	41	19	32	29	6	22	Not corrected for thermal polymer
7353	"	43	120	120	31	32	119	Not corrected for thermal polymer; final 75 hr at 120°C
7559	"	238	14	120	168	14	9	
4915	/2,2-dimethylbutane (57/43)	68	14	19	48	15	21	Not corrected for thermal polymer; assume 1:1 interaction
7367	/diphenylacetylene (36/64)	65	120	120	46	2	4	
7383	/diiodoacetylene (51/49)	24	120	120	17	82	375	Not corrected for thermal polymer; assume 1:1 interaction
Miscellaneous								
4914	Bis-(1,4-hydroxyethyloxy)-butyne-2	43	-75	-44	30	21	57	
4912	2-Butyn-1,4-diacetate	77	14	20	54	78	96	
1942	Diethylpropargylamine	42	-75	-36	30	2	5	
233	Ethoxyacetylene	40	-75	-38	28	2	13	
4921	Phenylpropargyl aldehyde	44	-73	-32	31	12	33	
4923	Phenylpropargyl aldehyde acetal	44	-73	-32	31	3	5	

⊕ In two component systems containing propiolic acid the G value is for propiolic acid disappearance.

* Run under nitrogen.

** Irradiated with Van de Graaff electrons, high dose rate (4000 megarep/hr).

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Radiation yields were not determined for acetylenedicarboxylic acid, a heat-sensitive solid monomer, since the monomer could not be distilled from the reaction mixture to determine the polymer formed. Other separation methods tried were also unsuccessful

Among esters there was generally fair radiation sensitivity with the monofunctional monomers and very high sensitivity among the polyfunctional monomers. Both neopentylene dipropiolate and pentaerythritol tetrapropiolate polymerized completely to infusible solids. A third polypropiolate, butyne dipropiolate, gave a 50% yield with $G = 100$. A similar monomer but containing only one double bond, butyne diacetate, gave similar results, $G = 100$. While the dipropiolate gave solid products, the diacetate yielded an oil. Among the halides, phenylbromoacetylene was the most sensitive ($G = 94$); propargyl chloride was second ($G = 34$).

In addition to the acetylenic derivatives borazole was radiolyzed in an attempt to form a dihydroborazole polymer which could be dehydrogenated to a polyborazole, a completely conjugated system. A radiation yield of $G = 10$ for polymer formation at ambient temperature indicated poor radiation sensitivity under the conditions used. A similar radiolysis with borazole containing 11.8% polymer indicated that radiation depolymerized the initial polymer.

D. CHEMICAL STRUCTURE CORRELATIONS   The screening program provided data which were used in studies designed to relate radiation sensitivity to chemical structure.

Six commercial acetylenic alcohols and four diols were radiolyzed to study the effect of structure modifications on polymerization. So far, changes in the hydrocarbon structure of these materials has not provided any strong leads. As summarized in Table IV, radiation yields were low. The polymers formed were of low molecular weight.

Structure/sensitivity studies on the propiolates are summarized in Table V. The monopropiolates gave only fair yields, while all of the polyfunctional propiolates appeared very sensitive. Propiolic acid is included for comparison.

The two acetylenic acids, shown below in Table VI, whose polymer analyses were determined, were very sensitive, indicating that the carboxylic acid group is a sensitizing group.
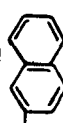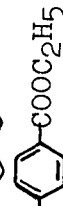
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TABLE IV

STRUCTURE/SENSITIVITY STUDIES FOR ACETYLENIC ALCOHOLS

$$HC\equiv\overset{R_1}{\underset{R_2}{C}}-C-OH$$

		Formula		Dose*,	Polymer	
					%	G
Run	System	R_1	R_2	megarep	Yield	Value
218	Propargyl alcohol	-H	-H	29	2	14
1905	1-Butyn-3-ol	-H	-CH₃	30	2	9
241	3-Methyl-1-butyn-3-ol	-CH₃	-CH₃	28	5	20
4902	3-Methyl-1-pentyn-3-ol	-CH₃	-C₂H₅	30	5	20
240	3,5-Dimethyl-1-hexyn-3-ol	-CH₃	-iso-C₄H₉	28 .	6	18
3448	1-Ethynylcyclohexanol	-Pentamethylene-		27	9	32

$$HO-\overset{R_1}{\underset{R_2}{C}}-C\equiv C-\overset{R_1}{\underset{R_2}{C}}-OH$$

Formula

		R_1	R_2			
219	2-Butyn-1,4-diol	-H	-H	29	9	40
3440	2,5-Dimethyl-3-hexyn-2,5-diol	-CH₃	-CH₃	46	3	6
3441	3,6-Dimethyl-4-octyn-3,6-diol	-CH₃	-C₂H₅	46	3	4
243	2,5-Diphenyl-3-hexyn-2,5-diol	-CH₃	-C₆H₅	48	11	10

*Radiolyzed with γ-rays in the solid state.

TABLE V

STRUCTURE/SENSITIVITY STUDIES FOR PROPIOLATES

$HC \equiv C-COOR$

Run	System	Formula R	Dose* megarep	Polymer % Yield	Polymer G Value
232	Propiolic acid	-H	28	35	204
4901	Methyl propiolate	$-CH_3$	30	4	20
1906	Ethyl propiolate	$-C_2H_5$	28	9	39
3410	Propargyl propiolate	$-CH_2-C \equiv CH$	29	12	43
3409	n-Butyl propiolate	$-(CH_2)_3-CH_3$	29	9	29
3414	sec-Butyl propiolate	$-C(CH_3)-CH_2CH_3$	29	8	25
3417	iso-Butyl propiolate	$-CH_2-CH(CH_3)_2$	29	5	17
3424	β-Naphthyl propiolate	[naphthyl]	47	15	18
244	p-Carboethoxyphenyl propiolate	[phenyl]$-COOC_2H_5$	62	36	30
4905	2-Butyn-1,4-dipropiolate	$HC \equiv C-COOCH_2-C \equiv C-CH_2OCO-C \equiv CH$	30	51	103
1941**	Neopentylene dipropiolate	$HC \equiv C-COOCH_2-C(CH_3)_2-CH_2OCO-C \equiv CH$	30	54	101
1928**	Pentaerythritol tetrapropiolate	$HC \equiv C-COOCH_2-C(CH_2OCO-C \equiv CH)_3$	30	100	113

*Radiolyzed with γ-rays in the solid state.

**Product - infusible solid

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TABLE VI

STRUCTURE/SENSITIVITY STUDIES FOR ACETYLENIC ACIDS

Run	System	Formula	Polymer % Yield	Polymer G Value
232	Propiolic acid	H-C≡C-COOH	35	204
3444	Phenylpropiolic acid	Ø-C≡C-COOH	43	73

A comparison of the substituted phenylacetylenes shown below in Table VII offers the most striking differences. Between the two halogen substituted phenylacetylenes, phenylbromoacetylene gave a G of 94 while phenyliodoacetylene irradiated under similar conditions gave a G of only 4.

TABLE VII

STRUCTURE/SENSITIVITY STUDIES FOR SUBSTITUTED PHENYLACETYLENES

Run	System	ØC≡C-R Formula ·R	Polymer % Yield	Polymer G Value
1933	Phenylbromoacetylene	-Br	45	94
3444	Phenylpropiolic acid	-COOH	43	73
4921	Phenylpropargyl aldehyde	-CHO	12	33
224	Phenylacetylene	-H	3	11
4923	Phenylpropargylaldehyde acetal	-CH(OC₂H₅)₂	3	5
4934	Phenyliodoacetylene	-I	3	4
214	Diphenylacetylene	-Ø	1	4

All of the substituted phenylacetylenes in Table VII were irradiated in the solid state for comparison purposes and with the thesis that ionic reactions would be predominate. As mentioned later, phenylacetylene may be easily polymerized to a solid by heat at 140°C even though it exhibits little tendency to polymerize at room temperature or below.

A more detailed investigation, which would include product identification, would be desirable and should throw light on the mechanism of radiation-induced acetylenic polymerizations.

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E. IRRADIATION CONDITIONS   Radiolytic polymerization processes have been shown to be dependent on such variables as temperature, state, dose, dose rate, purity, solvents, complexes, sensitizers, etc. It is possible that conditions can be found which favor acetylene derivative radiolytic polymerization to form long chain polyenes in reasonable yields. The problem is somewhat complexed by the fact that radiation yield and high molecular weight polymer formation are not synonomous. The latter is considered necessary in polyenes suitable for semiconductor use.

Neopentylene dipropiolate and propiolic acid, both sensitive to radiolytic polymerization, were studied as models to define optimum conditions for radiolytic polymerization to high molecular weight materials. With them, appreciable and measurable changes could be observed when controlling parameters were varied.

Our studies showed that polymerization of neopentylene dipropiolate is sensitive to temperature and state. A post-irradiation effect was also observed. These results and additional data are summarized below in Table VIII.

These data show the following trends.

1. Higher radiation yields are obtained by irradiating neopentylene dipropiolate solidified from the melt rather than material recrystallized from hexane.

2. A strong post-irradiation effect was observed in Run 1930: the product was fluid immediately after irradiation but further polymerized to a hard glass on standing at ambient temperatures for 24 hours. Run 3404 defines the yield under similar conditions, but the product was evaluated before post-irradiation effects could take place.

3. Dose rate had no appreciable effect on the radiolysis over the range of 0.7 to 3,700 megarep/hr.

4. Both temperature and state of the material during radiolysis seemed to affect the products and the yields. Runs made in the solid state yielded orange crystalline-like solids while those run in the melt yielded dark-brown glasses. The G values of the latter were undoubtedly conservative since the polymer yield was 95% or better. This follows since incremental radiation yields decrease with increasing conversion due to dilution of the reactants.

5. The monomer is thermally stable up to 90°C. It could not be polymerized with heat at 50°C (just below its melting point), in the liquid state at 70°C, or by peroxide-initiation at 90°C.

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TABLE VIII

IRRADIATION OF NEOPENTYLENE DIPROPIOLATE SYSTEMS

Run	System* (Form)	Irradiation Conditions Temp, °C Low	High	Dose, megarep	Polymer % Yield	G Value	Product
1941	NDP (solidified from melt)	-77	-36	30	54	101	Solid
3415	NDP (crystallized from hexane)	-79	-36	29	33	63	"
3430**	NDP (crystallized from hexane)	-75		37**	46	68	"
242	NDP (solidified from melt)	5	24	48	84	97	"
1910	NDP (pressed into pellet)	20	24	48	46	54	"
1923	NDP (crystallized from hexane)	20	25	48	37	43	"
1930	NDP (liquid)	65	65	30	95	177	Post-irradiation effect: red oil → gloss
3404	"	65	65	33	54	91	Red oil
1947	"	150	150	33	99	167	Red-brown glass
3403	"	150	150	33	100	165	Red-brown glass

*NDP = neopentylene dipropiolate

**Irradiated at 4×10^9 rep/hr with 2 Mev electrons

Propiolic acid, the most radiation sensitive material found in this study was examined under a number of conditions in an effort to increase the polymer molecular weight to form solid materials. The data are summarized in Table IX.

The wide range of radiation yields observed at low temperature indicates the sensitivity of the radiation-induced polymerization of propiolic acid to the irradiation conditions. Among the variables we consider important but have not yet completely defined are: purity; temperature profile during the irradiation; post-irradiation effects; and solid structure. The latter may be influenced by monomer purity and the method of freezing.

Some of the variables important in propiolic acid radiolysis were defined quite well, however.

Thus, irradiation at a high dose rate (3.7×10^9 rep/hr) with 2 Mev Van de Graaff electrons greatly reduced the polymer radiation yield to 25 from over 300 for the Co-60 gamma irradiated runs (7×10^5 rep/hr). This reduction was anticipated since radiation yields for chain reactions are dose-rate dependent. The product formed at this high dose rate was predominantly a black solid in contrast to the low molecular weight polymer obtained from gamma-radiolysis at low dose rate.

Irradiation to low doses with gamma-rays also greatly reduced the radiation yields and suggests an induction period. This is shown in the comparison (Table IX) of -78°C radiolytic polymerizations at 15 and 28 megarep doses. At the lower dose the G value was 31 vs. G values of 136 to 322 at the higher doses. Irradiations in the liquid phase were significantly lower than those observed in the solid phase, and these liquid phase radiolyses seem to be temperature independent from 20 to 100°C.

Significant thermal polymerization begins at 100°C and is not greatly enhanced by benzoyl peroxide. The thermally produced polymer is similar in appearance to that produced by radiolyses.

Also summarized in Table IX are a series of studies in which other materials were radiolyzed with propiolic acid. In these runs the radiation yields were based on acid-base titration values of the isolated polymer and of the recovered starting materials. In most runs a fair material balance was observed. Since some decarboxylation or carboxy group interactions may take place, these values should be considered tentative. The chemical yields obtained in these systems may be conservative since during the distillation of the higher boiling monomer some adducts of the lower boiling monomer may distill.

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TABLE IX

IRRADIATION OF PROPIOLIC ACID SYSTEMS

Run	System*	Irrad. Condition Temp, °C Low	High	Dose, megarep	PA % Yield	G Value	Remarks
232	PA	-75	-38	28	35	204	
1911	PA	-75	-34	28	55	322	5% of polymer is non-distillable
1916	PA	-74	-30	28	32	184	
4926	PA	-78	-40	29	24	136	
4936	PA	-75	-35	15	3	31	Irradiated at high dose rate (4000 megarep/hr)
3432	PA	-75		37	6	25	
4950	PA	-75		74	12	27	Irradiated at high dose rate (4000 megarep/hr)
7360	PA	14	39	115	34	49	Corrected for 7% thermally produced polymer
4927	PA	19	26	29	13	73	Time comparable for 30 megarep radiolysis
4933	PA	99	101	29	14	73	Time comparable for 30 megarep radiolysis
4938	PA	100	100	0	7		
4940	PA/benzoyl peroxide (99/1)	100	100	0	10		
1921	PA/t-butanol (49/51)	-74	-27	28	11	32	G(-butanol) = 36
1922	PA/water (50/50)	-74	-27	28	51	148	G(-water) = 182
3423	PA/acetonitrile (65/35)	-78	-37	30	21	76	G(-acetonitrile) = 72
4946	PA/phenylacetylene (34/66)	-78	-30	30	20	37	G(-phenylacetylene) = 50
7351	PA/diphenylacetylene (30/70)	-78	-30	30	1	1	G(-diphenylacetylene) = 18
1914	PA/sec-butyl propiolate (65/35)	-74	-30	28	51	194	G(-sec-butyl propiolate)=40
7364	PA/benzoquinone (99/1)	15	39	29	16	91	
7366	PA/ethyl ether (49/51)	15	39	29	14	36	G(-ethyl ether) = 12
7352	PA/maleic anhydride (42/58)	22	33	53	34	44	G(-maleic anhydride) = 52
4939	PA/polyethylene, ZPE (90/10)	26	35	29	8	48	25% of PA polymer bound to ZPE (material balance)
4944	PA/polyacrylonitrile PAN (90/10)	26	35	29	17	98	2% of PA polymer bound to PAN (material balance)
7368	PA/diiodoacetylene (43/57)	75	80	63	6	6	Not corrected for thermal polymer; G(-diiodoacetylene) = 38
7362	PA/phenylacetylene (41/59)	120	120	46	68	102	Not corrected for thermal polymer; G(-phenylacetylene) = 69

* PA = propiolic acid

The most striking differences are noted in the low temperature runs. Diphenylacetylene, itself a comparatively radiation-stable monomer, effectively stabilizes the sensitive propiolic acid. The polymer produced had only 3% titratable propiolic acid. On the other hand, water and sec-butyl propiolate both form sensitive systems with propiolic acid. Finally, acetonitrile, phenylacetylene, t-butanol, ethyl ether, and maleic anhydride form only moderately sensitive systems with propiolic acid. Among these later systems 1:1 interactions of propiolic acid with the second component was observed. With water, acetonitrile and t-butanol this 1:1 interaction appears to be the only reaction taking place. These 1:1 interactions could result from addition of a reactive hydrogen to the acetylene bond. In these cases the specific products were not defined. They could exist as 1:1 adducts or polymers thereof.

Since the polymerization was believed to be ionic, a high dielectric solvent, such as water, could improve the process. This should occur by solvation of electrons formed during ionization which would impede neutralization. Thus the positively ionized acetylene would have a longer life and enhance the polymerization. On the other hand, use of a solvent dilutes the energy absorbed by the acetylene thus lowering radiation yields. As mentioned above the results indicate a water-propiolic acid interaction, but still involving a chain process rather than homopolymerization of the propiolic acid.

Acetonitrile, a molecule which may react by dissociative capture with an electron, could trap electrons formed from the ionization of propiolic acid, thus increase the lifetime and probability of polymerization initiation by the positively ionized acetylene. In the acetonitrile/propiolic acid system, G values for the disappearance of both components were similar and indicated an equal molar interaction.

Benzoquinone, a free radical inhibitor, should lower the radiation yield of free radical reactions. This was not observed. Maleic anhydride is a well-known comonomer in free radical reactions and also is very reactive with diene systems. It was hoped that the maleic anhydride would react with the growing conjugated chain via a Diels-Alder addition. This could promote chain growth via reduction of termination via cyclization. Then a thermally induced reverse Diels-Alder would cleave maleic anhydride from the polymer molecule and produce the desired long chain polyene. Unlike all other propiolic acid runs, the maleic anhydride propiolic acid system gave all solid polymer with a 62% maleic anhydride content. The propiolic acid-maleic anhydride reaction product was evaluated but sufficient time was not available for the planned reverse Diels-Alder experiment.

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Grafting of propiolic acid to high density polyethylene (ZPE) and polyacrylonitrile (PAN) was attempted, to see if this technique would favor formation of a long chain polyene. In this case removal of the growing polymer from the reaction mixture could reduce chain termination. In both cases low molecular weight polymer predominated.

With polyethylene, despite the fact that the latter was not well-wetted by the propiolic acid, 8% of the propiolic acid was converted to polymer, of which 25% (2% of original acid) was bonded to the polyethylene. In contrast with polyacrylonitrile, which was swollen by the propiolic acid, 16% of the propiolic acid was converted to polymer of which only 2% (0.3% of original acid) was bonded to the polyacrylonitrile.

At 120°C, the propiolic acid/phenylacetylene system was radiation-sensitive. Part of this sensitization was due to a thermal reaction, since phenylacetylene, as was found later in this study, is quite thermally sensitive, completely polymerizing in 48 hrs at 140°C.

With the exception of the maleic anhydride/propiolic acid system, all other propiolic acid systems attempted (Table IX) failed to show large increases in polymer molecular weight, compared to homopolymerization of the acid.

Unlike propiolic acid, the radiation-induced polymerization of diphenylacetylene (Table III) does not appear to be sensitive to changes in state or in dose rate. In each case the radiation yields are quite low..

Phenylacetylene (Table III), also generally insensitive to dose rate and phase changes, is quite thermally sensitive above 100°C. The products from this system are solids, and from solubility data appear to be of low molecular weight. The thermally produced polymer is similar to that formed under radiolysis.

The effect of acetylene complexing agents on the radiolytic polymerization of acetylene derivatives was investigated using the methyl propiolate/pyridine system. Such complexes could favorably direct the polymerization by affecting the initiation and propagation steps. In addition, the type of polymer formed could be altered by changes in side reactions. Specifically, retention of the complex at the unsaturated bonds of the polyene could prevent their further reaction, and favor retention of conjugation in the chain.

Radiolysis of methyl propiolate and methyl propiolate/pyridine complexes (J. Chem. Soc. 1961, 3497) in 1:1 and 2:1 ratios were conducted for comparison, as summarized in Table X.

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TABLE X

LOW TEMPERATURE RADIOLYSIS OF METHYL PROPIOLATE/PYRIDINE COMPLEXES

Run	System*	Dose, megarep	Polymer %	G Value
4901	MP	29.7	3.7	20
3442	MP/Py (1:1)	27.2	5.2**	14
3443	MP/Py (2:1)	27.2	10.3***	10

*MP = methyl propiolate; MP/Py = methyl propiolate/pyridine

**Corrected for 17.3% solids formed in absence of radiation

***Corrected for 19.2% solids formed in absence of radiation

In general, irradiation conditions seem important but no consistent pattern has emerged. The dose rate, important with propiolic acid, has no effect with neopentylene dipropiolate. Temperature and state affect neopentylene dipropiolate, but similar large differences with β-naphthyl propiolate are not evident. Solvent effects with propiolic acid were inconclusive. Complexes may be very important for specificity and radiation sensitivity.

F. CHEMICAL AND PHYSICAL PROPERTIES   Very little work has been undertaken in this area since most of the products obtained have been oils. The thermal stability of neopentylene dipropiolate polymer, a high molecular weight, infusible, and insoluble material, was briefly studied. The glass-like material obtained by irradiating at 150°C was heated at 400°C for 5 hr under high vacuum. Over the interval, a considerable amount of volatile material distilled and the continued poor vacuum indicated extensive decomposition. Heating at 300 to 350°C for short intervals caused little decomposition.

Some attempts were made to distill the irradiated products under high vacuum and at moderate temperatures, so as to measure the higher boilers (residue). The data are summarized in Table XI.

As shown, only small amounts of materials were obtained as high boilers in most systems where monofunctional acetylenic derivatives were studied. Phenylpropiolic acid polymer was an exception, giving 85% high polymer. In all polypropiolate monomers, i.e. where the monomer had 2 or more acetylene groups, infusible solids were obtained, indicating high molecular weight materials.

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TABLE XI

DISTILLATION OF CERTAIN ACETYLENIC DERIVATIVES

Run	System	Polymer % Yield	Polymer G Value	% Non-volatiles in the Polymer 100°C	150°C	200°C
218	Propargyl alcohol	2	14		15	
1912	Propargyl chloride	3	18	77		
1911	Propiolic acid	55	322	10		
7364	Propiolic acid/benzoquinone	16	91		35	
1921	Propiolic acid/t-butanol	11	32	31		
3444	Phenylpropiolic acid	43	73		85	11
219	2-Butyn-1,4-diol	9	40		2	
1933	Phenylbromoacetylene	45	94			
4947	Diphenyl acetylene	18	10		1	
4905	2-Butyn-1,4-dipropiolate	51	103		97	
4912	2-Butyn-1,4-diacetate	78	96		21	18
4914	Bis-1,4-(hydroxyethyloxy)-butyne-2	21	57			50

G. ELECTRICAL PROPERTIES   Data on the electrical properties of the acetylenic monomers and their radiation-produced polymers, are summarized in Table XII. Properties measured included resistivity at ambient temperatures, resistivity as a function of temperature, and thermoelectric power.

For resistivity at room temperature, resistance was measured using rectangular pellets or powders. The values, dependent on the sample size, were normalized by use of the following relationship:

$$\rho_T = \frac{RA}{L}$$

where ρ_T is resistivity of the material at temperature T, R is measured sample resistance (ohms), A is sample cross-sectional area (in sq cm) measured perpendicular to the flow of current and L is sample length (in cm) or the distance between the electrical junctions. The resistivities of known organic semiconductors lie between 10 and 10^{19} ohm-cm.

Almost without exception in semiconductors, it is found that the resistivity, ρ, has a negative temperature coefficient and a linear relationship between $\ln \rho$ and $1/T$ which can be expressed as follows:

$$\rho = \rho_0 \exp (\epsilon/2kT).$$

ρ is the measured resistivity at a given temperature (ohm-cm), ρ_0 is obtained by extrapolating the resistivity when $1/T = 0$ which is characteristic of a given material, ϵ is the energy gap in electron volts, k is Boltzmann constant and T the temperature in °K. The factor of two, used in this expression, is commonly employed in organic semiconductor studies. The resulting energy term ϵ, obtained from the band theory, is the energy gap. This is usually related to the energy of production of charge carriers and is 1/2 the activation energy, E. The slope of log ρ vs. $1/T$ is proportional to ϵ, and values of 0.1 to 3 are common in organic materials.

It was recommended that electrical properties for evaluating polyenes be the same as those used for evaluating semiconductors such as silicon. Examination of the measurements normally made on semiconductors suggests that best comparisons should be done initially with resistivity and associated temperature coefficients.

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TABLE XII

ELECTRICAL PROPERTIES OF POLYENES

Run	System	History		Density gm/cc	ρ_{15}, ohm-cm		ρ_o, ohm-cm	ε eV	Q volt-deg
					air	vac			
1909-C	Acetylenedicarboxylic acid	Control	Pellet	1.5646	3.7×10^5	6.9×10^5			
1909	"	Irrad.	"		1.6×10^5	3.9×10^5			
1919-C	" , anhyd.	Control	"	1.501	3.7×10^6	6.4×10^6			
1919	" "	Irrad.	"	1.599	9.9×10^6	1.1×10^7			
1918-C	Acetylenedicarboxylic acid monopotassium salt, anhyd.	Control	"	1.6289	5.0×10^9	5.0×10^9			
1918	"	Irrad.	"		5.4×10^9	5.4×10^9			
1910-C	Neopentylene dipropiolate	Control	"	1.1343	4.8×10^8	4.8×10^8			
1910[a]	"	Irrad. (pressed before irrad.)			9.4×10^8	1.2×10^9			
1910	" , washed	Irrad.			4.0×10^{10}				
1924	" , recryst.	Control		1.262	4.9×10^{12}		1.4×10^7	0.634	0
1947	" "	Irrad.	Glass	1.208	6.6×10^{11}		none	none	0
1923	" "	Irrad.	Powder		3.9×10^{12}				
4919	Diiodoacetylene	Thermal	Crudely shaped mass		3.7×10^7				
4925-C	"	Control	Powder		7.9×10^{11}				
4925	"	Irrad.	"		1.2×10^{13}				
3444-C	Phenylpropiolic acid	Control	Pellet	1.235	3.0×10^6				
3444	"	Irrad.	"	1.345	6.4×10^6				
3442	Methyl propiolate/pyridine (1/1)	" , crude shape			7.5×10^7				
3443	" (2/1)	"			3.7×10^7				
1928	Pentaerythritol tetrapropiolate	"	Powder		1.8×10^{10}				
4905	2-Butyn-1,4-dipropiolate	"	"		3.1×10^{10}				
7367	Diphenylacetylene/phenylacetylene	"	Pellet		3.7×10^9				
4947-C	"	Control	"		5.3×10^{11}				
7361	Phenylacetylene (benzene/methanol insoluble)	Ir ad.	"		8.6×10^9				
7361	" (" / " , soluble)	"			2.9×10^9				
7383	" /diiodoacetylene	"	Powder		2.0×10^9				
3413	Acetylenedicarboxamide	"	Pellet		2.0×10^{11}				
4950	Propiolic acid	"	Powder		5.4×10^{10}				
4939[b]	Propiolic acid/polyethylene	"	Pellet		2.0×10^{10}				
4944[c]	Propiolic acid/polyacrylonitrile	"	"		4.8×10^{10}				
7352	Propiolic acid/maleic anhydride	"	"		3.5×10^{10}				
7362	Propiolic acid/phenylacetylene	"	"		1.9×10^{11}				
7368	Propiolic acid/diiodoacetylene	"	Powder		4.8×10^{10}				

[a] Product contained 54.5% of monomer
[b] Product contained 22.3% polypropiolic acid
[c] Product contained 1.92% polypropiolic acid

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As shown in Table XII electrical resistivity was the chief property determined. Other properties, such as resistivity as a function of temperature, Seebeck effect, photoconductivity, etc. were not measured on all samples, since the resistivity values found were too large to warrant these additional measurements. Resistivity vs. temperature measurements on monomeric and polymeric neopentylene dipropiolate showed a negative temperature coefficient with an energy gap of 0.634 ev for the monomer. No temperature coefficient was observed with the polymer. Attempts to measure a thermoelectric emf, or Seebeck effect, on neopentylene dipropiolate before and after irradiation at high temperature have failed with no thermal emf detected.

In this study a tentative goal of 10^3 ohm-cm was set for resistivity values. Actual values obtained ranged from 1.6×10^5 to 1.18×10^{13} ohm-cm. Sufficient solid samples were not obtained to permit detailed definition of those structures which would lead to resistivities equal or lower than the desired goal. However the following important patterns are evident from the results in Table XII:

1. The resistivity is highly dependent on the state of the material. Neopentylene dipropiolate monomer pellets prepared from fused material had resistivity values 10^4 fold lower than pellets prepared from small crystals. Similarly, polydiiodoacetylene in a large mass gave resistivity values 3×10^5 fold smaller than those of a powdered sample.

2. Resistivity values of certain monomeric acetylene derivatives are strikingly low for organic materials, e.g., phenylpropiolic acid and acetylenedicarboxylic acid.

3. Polymerization of the acetylene derivatives does not lead to appreciable changes in resistivity values; e.g., acetylenedicarboxylic acid, acetylenedicarboxylic acid monopotassium salt, neopentylene dipropiolate, and phenylpropiolic acid.

4. Resistivity values of polymers of acetylenedicarboxylic acid, diiodoacetylene, phenylpropiolic acid and methyl propiolate/pyridine complexes ranged from 10^5 to 10^8 ohm-cm and are considerably lower than polymers from polypropiolates, phenylacetylene, diphenylacetylene and acetylenedicarboxamide.

These results suggest the following potentially fruitful areas for obtaining polymers of low electrical resistivity: phenylacetylene polymers with carboxyl substituents on the phenyl group and polymers from diethynyl aromatics. Modifications of the former type by operation on the carboxyl group of the formed polymer could lead to selection rules for improving resistivity.

Various polyvalent metals appear to be good possibilities. With diethynyl aromatics, the polyfunctional monomers could lead to cross-linked high melting solid materials with large uninterrupted conjugation. These would contrast with the polypropiolate polymers which also cross-link to high melting solids but whose conjugation is interrupted by the non-conjugated alkyl portion of the molecule. The resistivity values of 10^8 to 10^{10} for these polypropiolates suggests that substantial resistivity reductions may be possible by use of completely conjugated groups connecting the acetylene functions.

IV. EXPERIMENTAL

A. CHEMICAL SYNTHESIS

1. Butyl Propiolate   To a 500-ml flask was charged 100 ml benzene, 14.0 g (0.2 mole) of previously distilled propiolic acid, 16.6 g (0.22 mole) of n-butanol and 0.1 g p-toluenesulfonic acid. The flask, equipped with a stirrer, Dean-Stark trap, and condenser, permitted water removal azeotropically. Refluxing 15 hr gave 2.8 ml water, indicating a 74% yield. After washing the reaction mixture with water and distilling the solvent benzene, further distillation yielded 18.3 g (73%) n-butyl propiolate, n_D^{25} = 1.4211.

Isomeric butyl and other propiolates were also made by this procedure and are listed below:

Compound	% Yield	n_D^{25}	B.P. °C	mmHg
sec-Butyl propiolate	30	1.4220	25	0.05
iso-Butyl propiolate	56	1.4170	25	0.05
Propargyl propiolate	28	1.4445	55-56	7.60
Methyl propiolate	36	1.4742	31	0.65
2-Butyne-1,4-dipropiolate	14		110-120	0.05

2. Neopentylene Dipropiolate   This material was prepared on a large scale (0.75 mole) by a procedure similar to that described above. To 110-ml benzene was added 78 g (0.75 mole) of 2,2-dimethyl-1,3-propanediol, 100 g (1.43 mole) of propiolic acid and 1 g of p-toluenesulfonic acid. The 25 ml water obtained indicated a 97% yield. After the benzene solution was water-washed, distillation gave 134 g (89%) neopentylene dipropiolate. (Previous Monsanto experience has shown that extreme caution is required in the large-scale distillation of pure propiolate esters, since violent explosions may occur.) The product was further

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purified by two recrystallizations from n-hexane to produce white needles, m.p. 61-62°C. Numerous distillations of pure material on a 1-2 g scale under high vacuum have been conducted with no explosions.

3. Phenylbromoacetylene   Using the procedure of Truce, et al., J. Am. Chem. Soc. 78, 2760 (1956), phenylacetylene (10 g, 0.098 mole) was slowly added to a sodium hypobromite solution formed by the slow addition of 160 g (1 mole) bromine to 120 g (3 mole) sodium hydroxide in 250 ml water. After stirring for two hours, the mixture was extracted with ether, the ether layer was dried with MgSO$_4$, and distilled to yield 3 g (11%) of phenylbromo-acetylene, b.p. 49-52°C/4 mm, and n_D^{25} 1.6045.

4. Phenyliodoacetylene   To a 1000-ml 3-neck flask equipped with a mechanical stirrer and a dry ice condenser was added 25 g (0.1 mole) of iodine. After cooling the flask in a liquid ammonia bath, 500 ml of liquid ammonia was quickly added to the flask with vigorous stirring. To this stirred solution was added dropwise 21 g (0.2 mole) of phenylacetylene in 25 ml of ethyl ether. The ammonia solution, dark green and containing solids, after 2 1/2 hr became clear-yellow. The cooling bath was removed and the solution was allowed to evaporate to about 50 ml. This solution was poured into a mixture of 200 ml water and 200 g of ice. The product separated as a red oil. This red oil was washed with 100 ml of 15% sodium thiosulfate solution and then with water. The crude yield of oil was 30.4 g (0.13 mole), 65%, n_D^{26} = 1.5992. A small quantity was purified via distillation and gave a yellow liquid, b.p. 80-90°C/0.1 mm, $n_D^{25.5}$ 1.6324 (lit n_D^{25} = 1.6591).

5. Phenylpropiolic Acid   Using the procedure of Abbott and Althansen, Org. Synthesis, Coll. Vol. II, page 270, and Abbott, Org. Synthesis, Coll. Vol. II, page 515, phenylpropiolic acid was prepared starting with ethyl cinnamate. One mole, 159.8 g, of bromine was added in small portions with stirring to a cooled solution of 176.2 g (1 mole) of ethyl cinnamate in 100 ml carbon tetrachloride. After standing one hour, part of the carbon tetrachloride was evaporated to precipitate ethyl α,β-dibromo-β-phenylpropionate, which after air-drying, weighed 276.6 g (82% yield). The dibromo ester, 252 g (0.75 mole) was dehydro-brominated and hydrolyzed with hot alcoholic potassium hydroxide (189 g KOH in 900 ml of 95% ethanol) for 5 hr. After neutraliz-ing the solution with concentrated hydrochloric acid and filter-ing the precipitated salts, the ethanol was removed by distil-lation. The distillation residue and accompanying precipitated salts were dissolved in 800 ml water, cooled with ice, and acidified with excess 20% sulfuric acid. The precipitated phenylpropiolic acid was filtered with suction. Purification was effected by treating an alkaline solution with decolorizing

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carbon, precipitating the acid with sulfuric acid, and recrystallizing the phenylpropiolic acid from carbon tetrachloride. The yield of white needles was 27 g (25%). An additional 24 g (22%) was obtained from the mother liquor.

6. Propiolyl Chloride   Propiolic acid, 70 g (1.0 mole), and 281 g (2.0 mole) benzoyl chloride was charged to a 500-ml flask containing a thermowell. The flask was quickly attached to an 8-inch Vigreux column and distillation head fitted with a calcium chloride drying tube. The flask was heated rapidly until distillation began (~30°C head temperature), and then the heat was reduced to a minimum consistent with steady distillation. Flask temperature was not allowed to exceed 200°C. The distillate collected was immediately redistilled through the same column yielding 16.7 g (18.4%) of propiolyl chloride, a colorless liquid, b.p. 55-56°C; n_D^{25} 1.4191. Propiolyl chloride is highly volatile, lachrymatory and potentially explosive. It is stable up to several weeks when stored at -10°C.

7. Acetylenedicarboxamide   Using the procedure of Blomquist and Wilson, J. Org. Chem. 10, 149 (1945), acetylenedicarboxamide was prepared by the careful addition of 20 g dimethyl acetylenedicarboxylate (0.14 mole) to a vigorously stirred 80 cc of concentrated ammonia solution cooled at -10°C. Stirring was continued for one hour longer. The precipitated amide was filtered, washed with 20 ml ethanol and dried 7 days in a vacuum desiccator. A 12.5 g (78%) yield of the dry amide, m.p. 196-205°C, was obtained.

8. Diiodoacetylene   An attempt to prepare diiodoacetylene by the method of Dehn, J. Am. Chem. Soc. 33, 1598 (1911), failed. The method consists of adding a sodium hypochlorite solution and acetylene to a potassium iodide solution. (Air must be rigidly excluded since even traces will ignite the dichloroacetylene by-product which forms on the dropping funnel containing the hypochlorite solution.)

The method of Vaughn and Nieuwland, J. Am. Chem. Soc. 54, 787 (1932), was successful. Liquid ammonia, 750 ml, was added as rapidly as possible to 100 g (0.79 mole) iodine in a cooled 2-liter flask equipped with a stirrer and a dry ice reflux condenser. The reaction was quite violent and some iodine vapor was lost. Acetylene was then bubbled rapidly into the solution. A 4-8 mm glass tube was used for the acetylene inlet to prevent clogging at the inlet. After 2-1/2 hr the solution cleared, indicating the end of the reaction. The flask was heated on a steam bath to evaporate the ammonia to a volume of 150 ml.

The addition of 500 ml of water precipitated diiodoacetylene, which was filtered with suction and pressed dry with a sheet of rubber. The moist diiodoacetylene was dissolved in 300 ml n-hexane, the solution was dried over calcium chloride, decanted, cooled with dry ice and the crystallized diiodoacetylene was filtered through a cold funnel. A 30 g (54%) yield of dried white crystals, m.p. 77-79.5°C, was obtained. An additional 8 g (14%) of product was obtained by crystallization from the mother liquor. Diiodoacetylene sublimes under vacuum and will explode on impact or friction. In a sealed tube the diiodo-acetylene exploded at 110°C, yielding what appeared to be iodine and carbon.

9. <u>Phenylpropargyl Aldehyde</u>   Using the procedure of Allen and Edens, Org. Synthesis, Coll. Vol. III, page 731, phenyl-propargyl aldehyde was prepared starting with cinnamaldehyde. A solution of 44 g (0.33 mole) of cinnamaldehyde in 167 ml of acetic acid was charged to a 500-ml flask equipped with a reflux condenser, stirrer and dropping funnel. After cooling to 0°C, 53.5 g (0.33 mole) of bromine was added with vigorous stirring, followed by 23 g (0.17 mole) of anhydrous potassium carbonate. After evolution of CO_2 had ceased, the mixture was refluxed for 30 minutes, cooled and poured into 435 ml of water. The crude precipitated α-bromocinnamaldehyde was filtered and recrystal-lized from aqueous ethanol. The yield was 46 g (66%), m.p. 70.5-74°C.

A mixture of 45 g (0.21 mole) of α-bromocinnamaldehyde, 50 ml (0.3 mole) of ethyl orthoformate, 40 ml of absolute ethanol and 0.5 g of ammonium chloride was refluxed 30 minutes and distilled, giving 50.5 g (83% yield) α-bromocinnamaldehyde acetal, n_D^{25} 1.5360.

Dehydrobromination was effected by refluxing 50 g (0.18 mole) of the α-bromocinnamaldehyde acetal with ethanolic potassium hydroxide (21 g potassium hydroxide in 200 ml absolute ethanol) for 1.5 hr. After adding 1.5 liters of water, an oil separated and the mixture was extracted with three 170-ml portions of chloroform. The chloroform solution was washed with three 75-ml portions of water and dried over sodium sulfate. Dis-tillation (after removing the chloroform) gave 31.3 g (90% yield) of phenylpropargyl aldehyde acetal.

Phenylpropargyl aldehyde acetal, 29 g (0.14 mole), was converted to the aldehyde with 150 ml 2.4N sulfuric acid, by heating on a steam bath for 30 minutes with occasional shaking. The aldehyde was steam-distilled, extracted from the distillate with ether, and the ether solution was dried over sodium sulfate. During distillation, the major part of the aldehyde polymerized to a solid resin, the yield being 1.1 g (6%).

10. **Attempted Syntheses**   The following syntheses were attempted unsuccessfully:

1. Dicyanoacetylene by dehydration of the diamide with P_2O_5.

2. o-Cyanophenylacetylene from o-cyanocinnamic acid.

3. 3-Chloro-1-butyne from the corresponding alcohol using thionyl chloride or a zinc chloride-hydrochloric acid mixture.

4. Neopentylene diphenylpropiolate, phenylpropiolate, t-butyl propiolate, 1,5-naphthylene dipropiolate, and 1,4-phenylene dipropiolate by acid-catalyzed esterifications from the corresponding acids and dihydroxy compounds.

B. SAMPLE PREPARATION   Most of the irradiations were conducted in glass break-seal tubes. These tubes, 14 mm diameter/10 inch over-all length, were fitted at each end with standard taper joints to enable filling and breaking while attached to the vacuum manifold. This allowed strict control of the atmosphere over the sample during the irradiation and while opening the break-seal after irradiation.

The normal operation involved attaching the open end of the break-seal tube to the vacuum line and evacuating the system. Distillable samples were distilled from another part of the vacuum line into the break-seal tube. Nondistillable solids were loaded into the break-seal tubes before attachment to the vacuum line. While under high vacuum, the tube was sealed off with an oxygen-gas torch. After irradiation the break-seal end of the tube was loaded with a small iron bar and then attached to the vacuum line. After the system was evacuated, the break-seal was opened using a magnet to operate the iron bar for rupturing the seal. The gas volumes were measured by noting the pressure rise in the closed system.

C. EVALUATION OF IRRADIATED SAMPLES   When possible the initial monomer was distilled from the residue and the weight of residue was reported as polymer. In other cases, the residue remaining after the irradiated sample had been extracted with an appropriate solvent in a Soxhlet apparatus was considered as polymer. In a few cases an aliquot of the irradiated sample or some of the residue obtained from an ordinary distillation was distilled at several temperatures under high vacuum with a microstill. In this way a crude separation of low molecular weight polymer, dimer trimer, etc., was made from high molecular weight polymer.

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Visual, chemical and physical observations were made on the irradiated samples and on the resulting polymers.

Electrical resistivity measurements were made on all solid polymers, either as powder or pressed pellets. Before pressing into pellets, the products were tested for shock and pressure-sensitivity with the impact tester described below. Pellets, 1x0.2x0.2", were formed in a pellet press at 10 to 50,000 psi. Silver paste contacts were made on the pellets and spring loaded platinum contacts were used for all the powders. Resistance was measured with a General Radio Megohm Bridge (Model 544B). As described in D-8 below (Figure 12), pellet samples were mounted in a special holder which permitted measurements at varying temperatures under atmospheric or vacuum conditions. Thermo-electric power measurements were conducted in the apparatus described in section D-7 below (Figure 11).

D. EQUIPMENT

1. Vacuum-Line   A vacuum-line (Figure 1) was constructed for sample preparation and purification, loading irradiation vessels, and work-up of radiolyzed materials. The system was set up in a hood. It consisted of a Welsh vacuum pump coupled to an oil diffusion pump and a 24-mm manifold. Connected to the manifold was a sample loading, purification and work-up system designed to handle the synthesis and work-up problems visualized.

2. Impact Tester   A device for safely determining the impact and pressure sensitivity of solids (Figures 2 and 3) was designed and built. This device is essentially a small pellet press made to allow for escaping gases. The rubber "O" ring at top helps to direct the force of even a glancing blow into a vertical direction to the dowel pin. If an explosion occurs, the gases are vented between the body and the lower cap. The cap inserts at each end and the 1/8" dowel pin are of hardened steel. By placing a small amount (<0.01 g) of sample in the assembly behind a shield and striking, a small explosion can be safely detected. Forces of about 100,000 psi can be used, which is 10-fold the pressure used to make pellets for electrical measurements.

3. Pellet Press   The pellet press is shown in Figure 4. A 1-g sample yields a pellet 1x0.2x0.2". Generally, pellets are formed under 10,000 psi by use of a 50,000 psi hydraulic press.
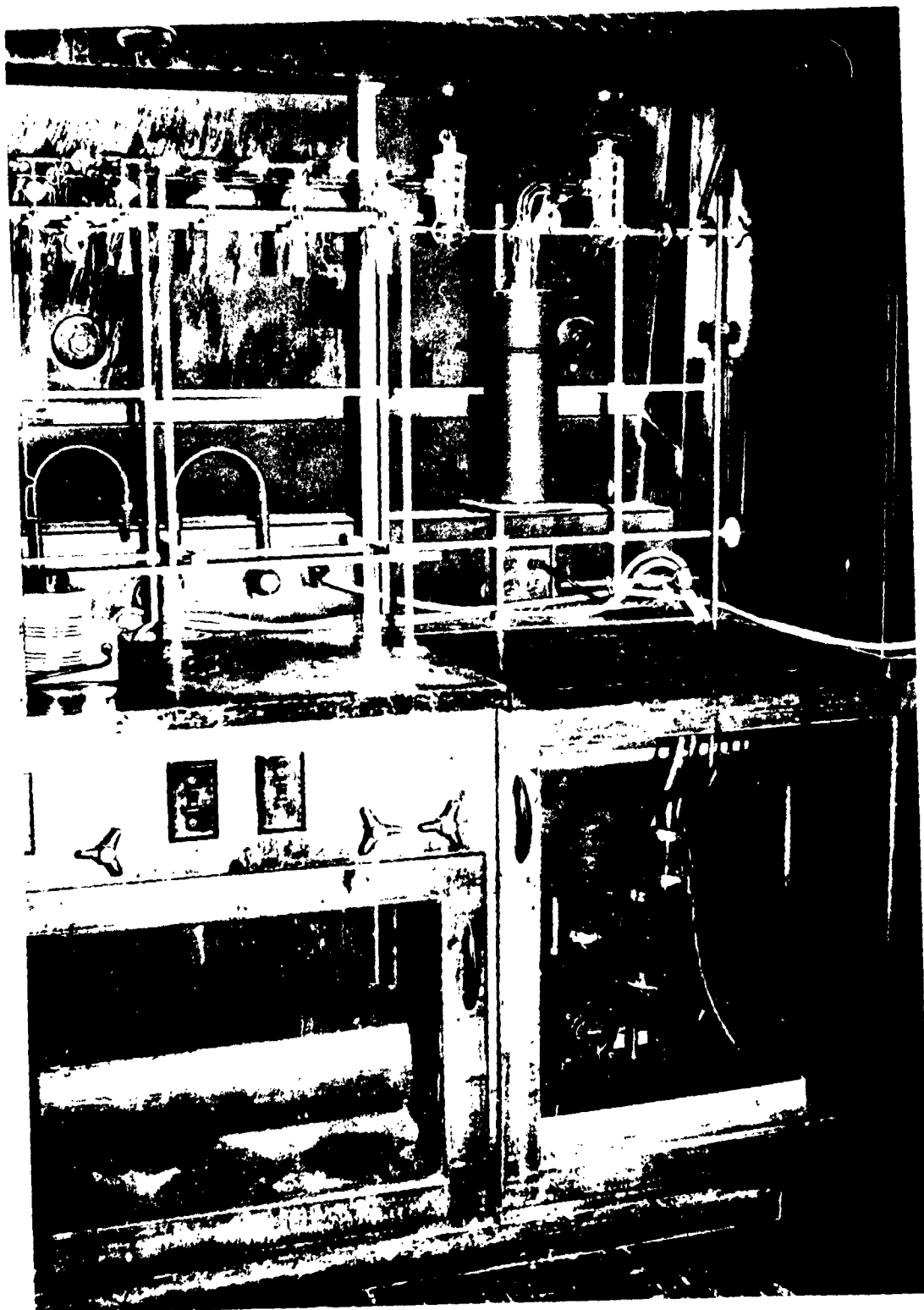
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Figure 1. Vacuum System for Manipulation of Samples
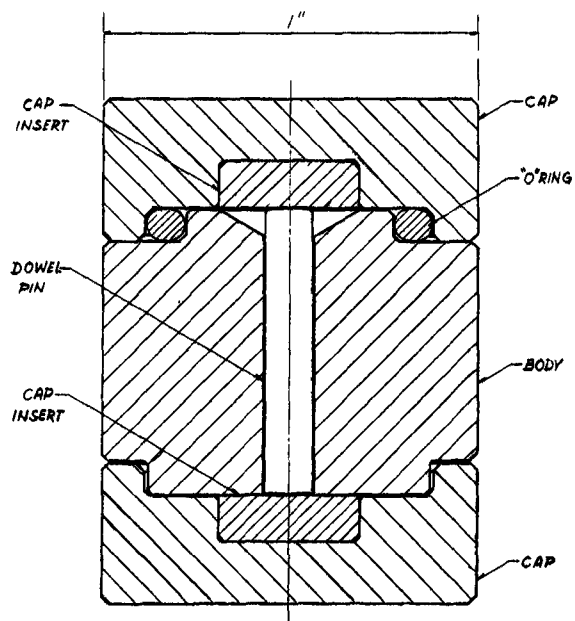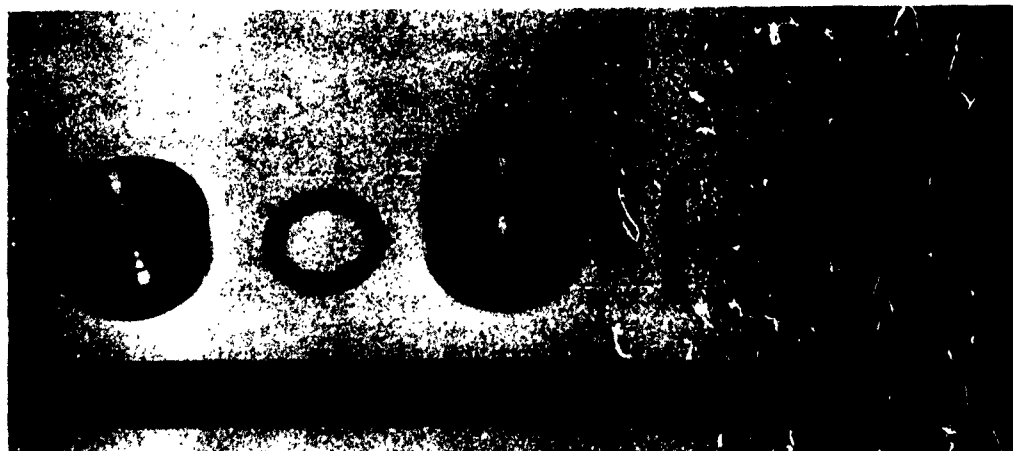Under Controlled Atmospheres

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Figure 2.   Impact Tester, Schematic

Figure 3.   Impact Tester
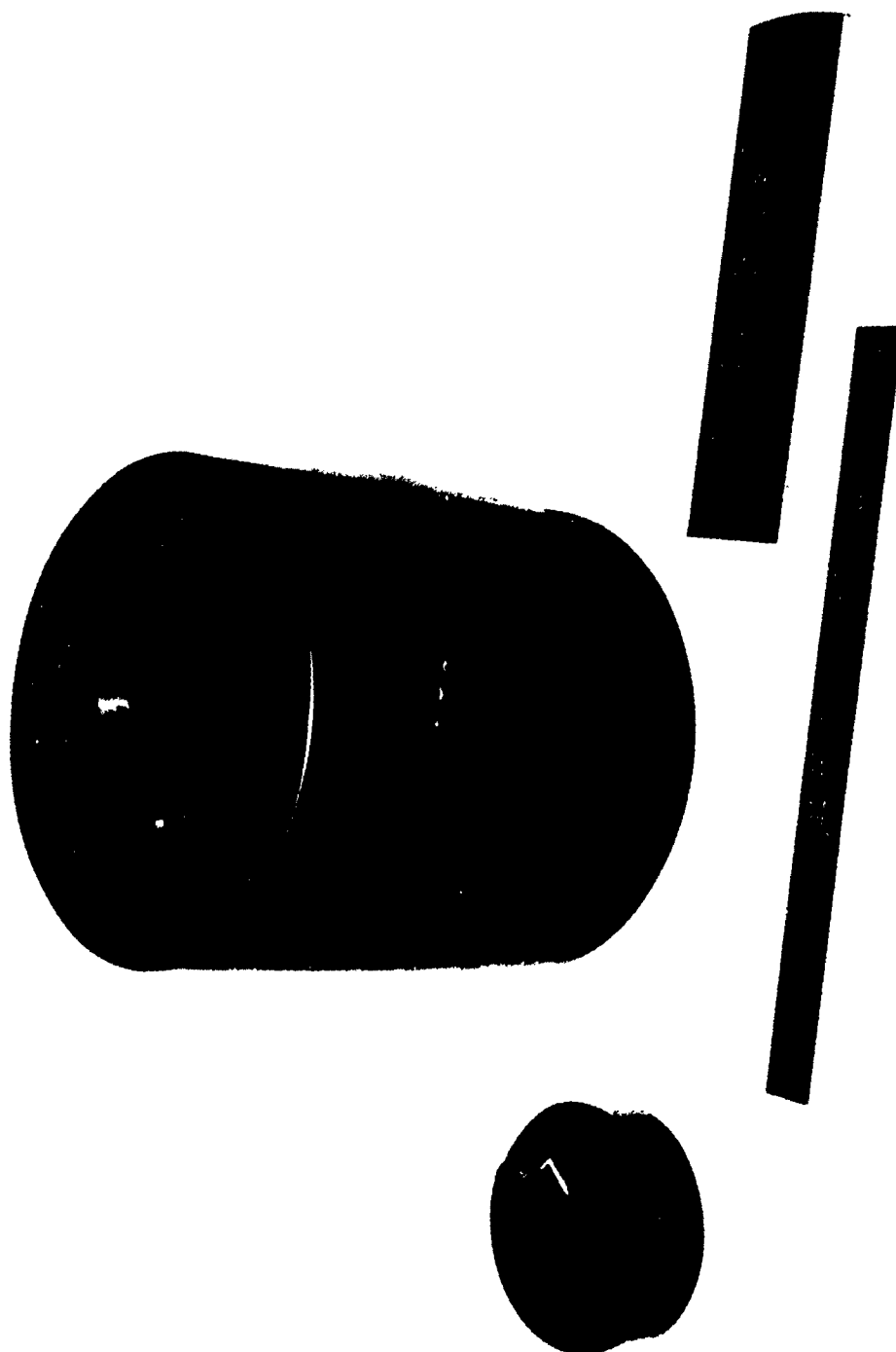
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Figure 4. Pellet Press

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4. **Irradiation Chamber** A special irradiation chamber (Figure 5) was designed and built to permit γ-radiolysis of 1- to 5-g samples at varying temperatures. As shown, the unit consists of a center stainless steel tube, 15 mm ID and 15 in. high, open at the bottom and closed at the top. When in operation, the Co-60 source, described later, may be driven up into this center tube for irradiations. The cuplike device at the bottom of this tube centers the tube in the reactor "pig" and together with the outer 5-inch diameter sleeve acts as a container for dry ice or insulation. Also shown in Figure 5 is a turret of five copper tubular sample holders, 1 in. OD, 10 in. high, and closed at the bottom, which have been soft-soldered together. This turret fits snugly over the center source tube so that when in place each tube is identical in geometry with respect to the Co-60 source. Temperature is measured with thermocouples placed either inside one of the copper tubes or between the turret and the center source tube.

5. **Co-60 Source** Radiation was emitted from a 590-curie Co-60 source (Figures 6-10). This source was made up of a 2-inch stack of 1-cm dia. metal discs sealed in a stainless steel capsule (Figure 8). Similar discs, 2.5 in. high, made from Mallory metal, are also sealed inside the capsule so when the capsule is in a vertical position the Mallory metal discs lie on top of the cobalt. The capsule is stored in a 24-in. dia./26-in. high lead storage pig which rests on a 5-ft metal stand. A 30-in. dia./26-in. high lead-filled cylinder with a 9-in. diameter center hole rests on top of the cobalt storage pig. This 9-in. cylindrical void is partially filled with a heater assembly, leaving a 5-in. cylindrical void for a reaction vessel, namely the irradiation chamber previously described.

The over-all unit is pictured in Figure 6, while Figure 8 details the storage cylinder and capsule and Figure 9 the top radiation shield and heater. The irradiator is operated in a vertical position as shown in Figure 6. The cobalt capsule is attached to a rod which in turn is attached to a rack. This rack is contacted with a pinion attached to a rod extending through the wall to the control panel (Figure 7) in the galley. Thus, by operation of a turning wheel attached to this rod, the source can be remotely elevated or lowered with the rack and pinion mechanism.

Also shown in Figure 8 is a specially designed top shield for the storage pig. This shield reduces the upward component of the source's γ-radiation. This shield consists of a rotating 3.5-in. dia./7-in. lead cylinder controlled by a rod attached to a wheel at the base of the storage cylinder. When the lead shield is rotated over the Co-60 source, the γ-ray intensity at the reaction chamber top is reduced to <1 mr/hr. At this level, the chamber can be loaded manually.

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Figure 5. Irradiation Chamber Showing Center Source
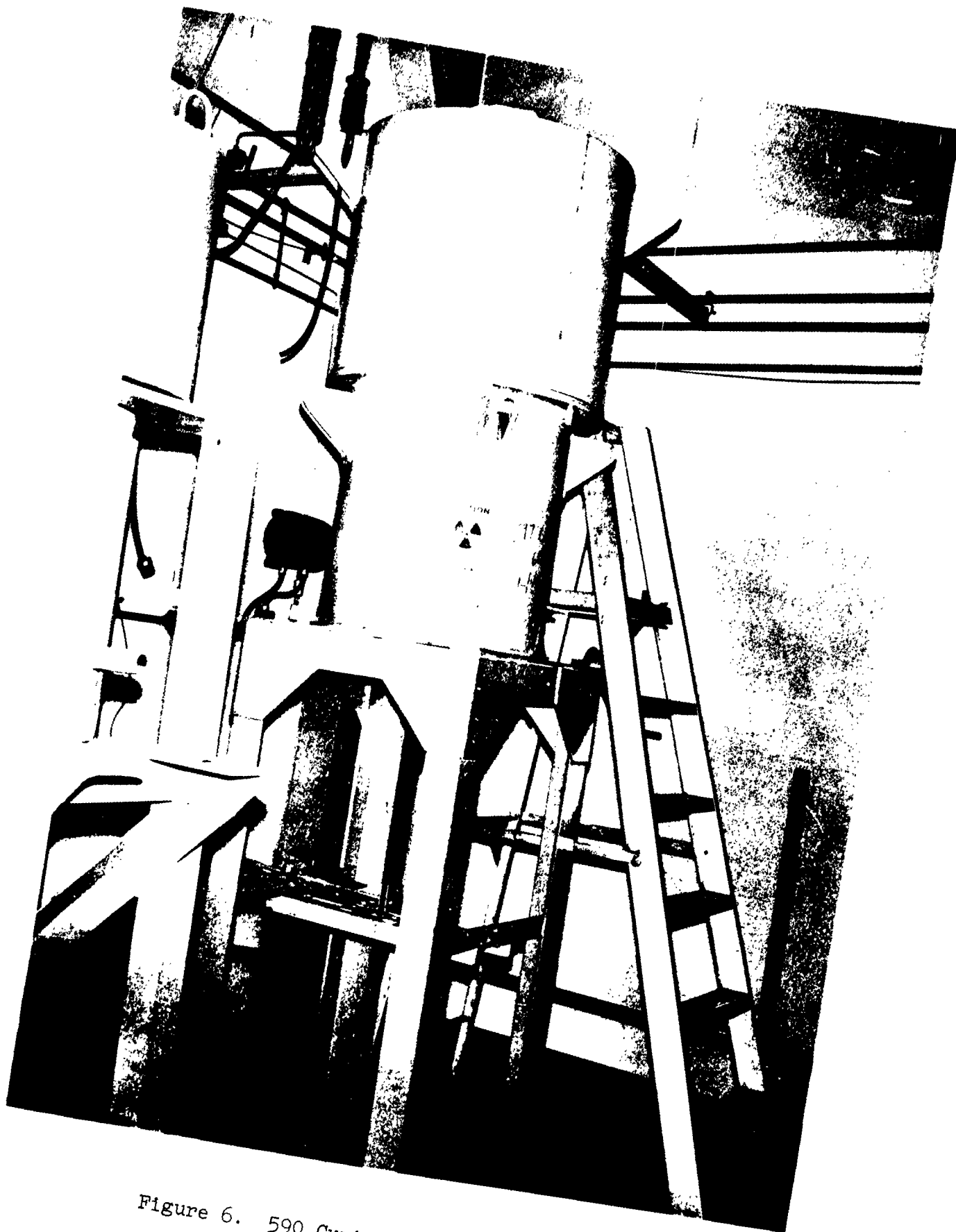Tube, Turret of Sample Tubes, and Outer
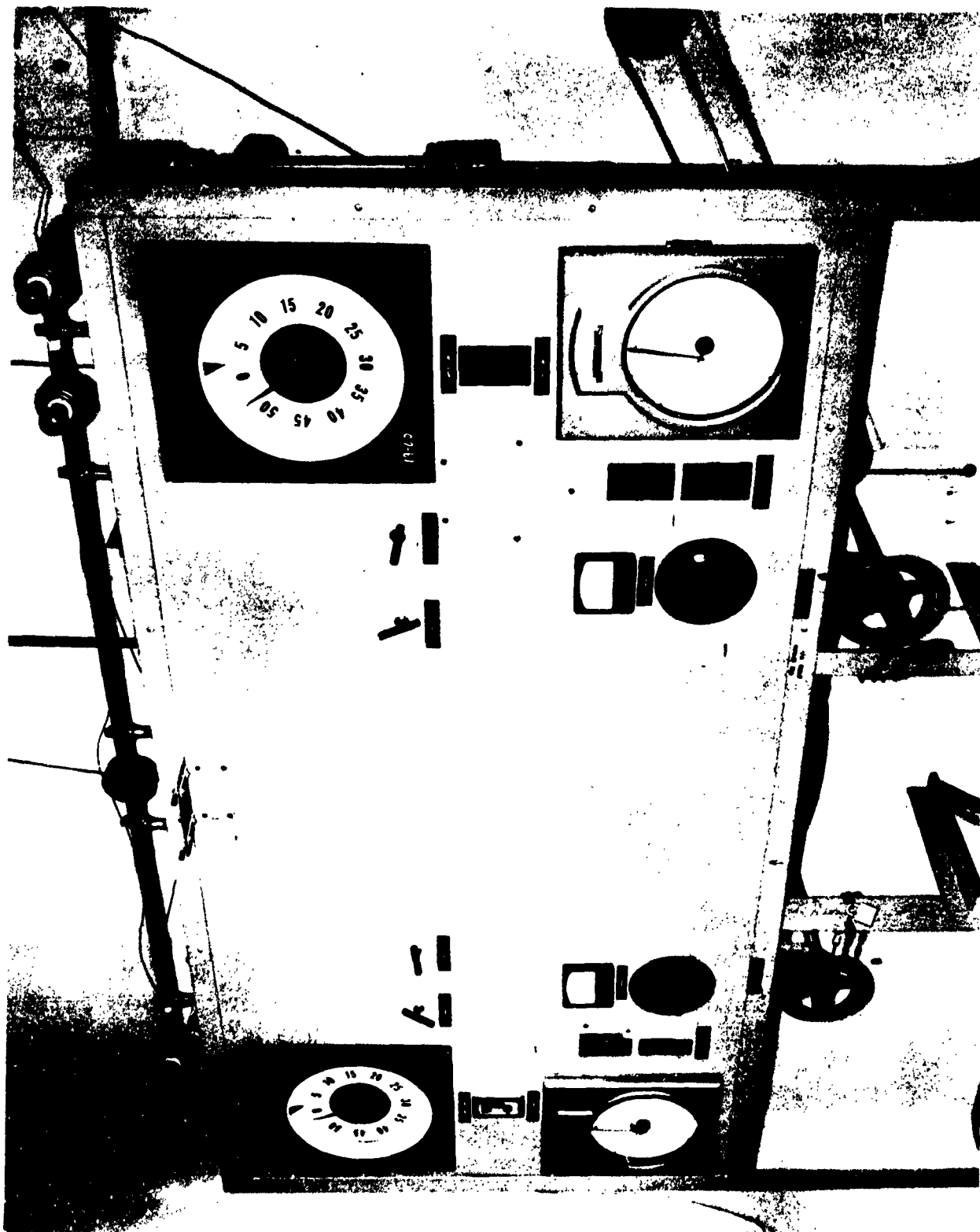Sleeve

39

Figure 6.   590 Curie Co-60 Source Housing

Figure 7. Panel Board With Controls and Instrumentation

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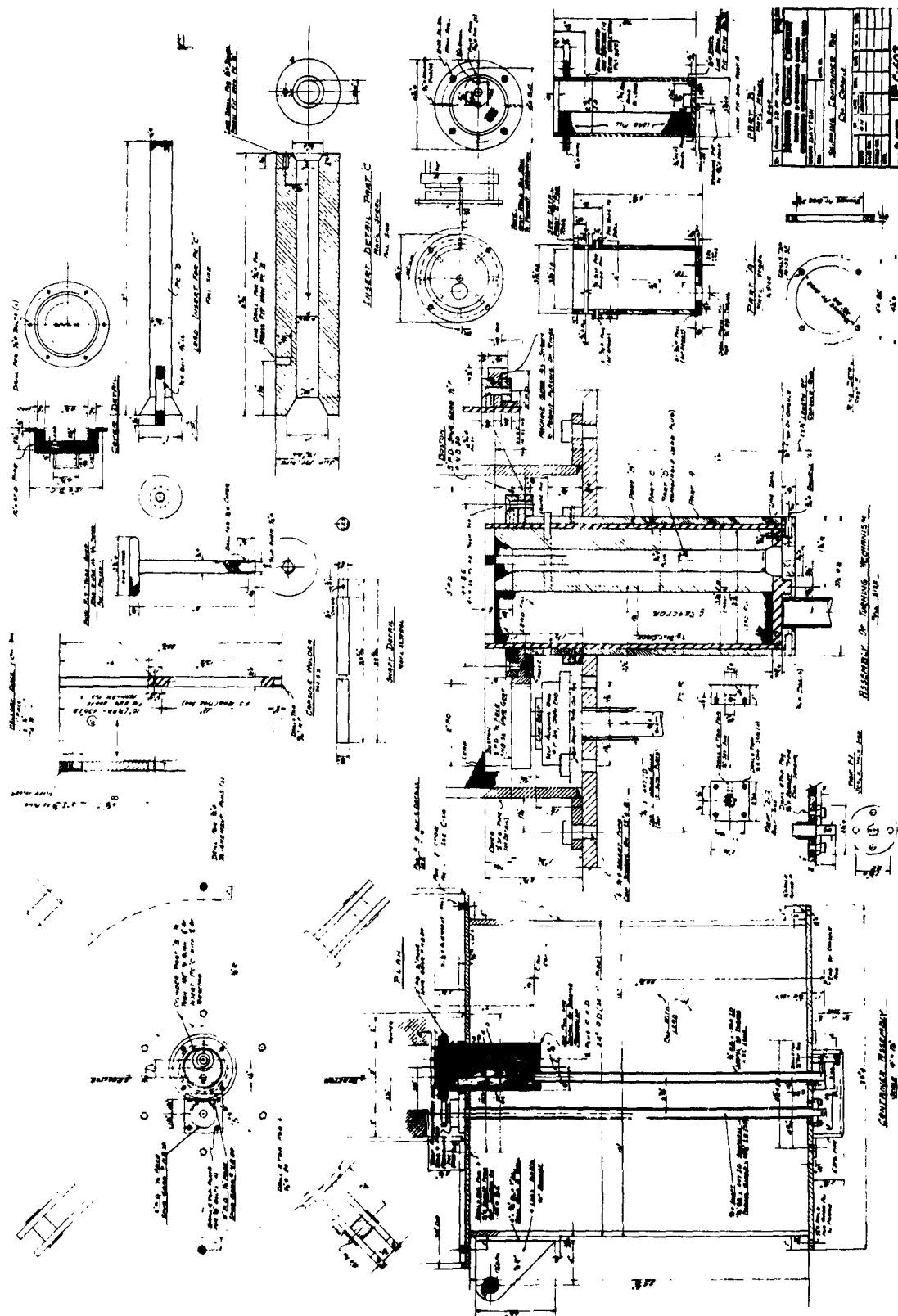
Figure 8. Storage Container for Co-60 Capsule
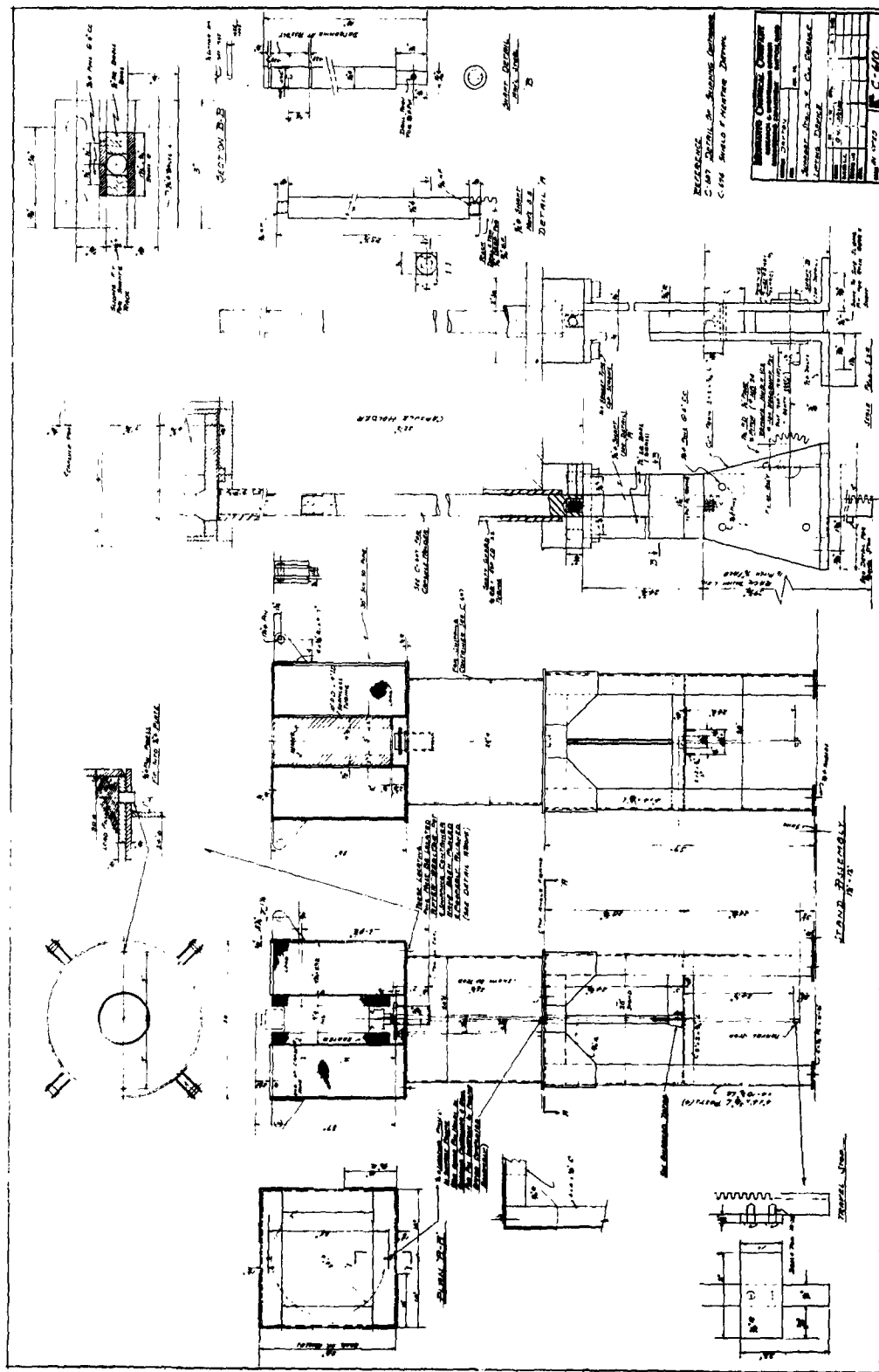
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Figure 9. Reactor Shield and Heater for Co-60 Capsule

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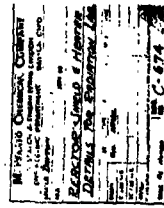
Figure 10. Support Stand and Co-60 Capsule Lifting Device

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The entire unit (Figure 6) is housed in a specially designed room having 1-ft thick concrete walls. Controls for this unit (Figure 7) are located in an adjacent galley. The panel board provides temperature and source control as well as pressure control for closed systems.

6. Dosimetry   The dosimetry of the sample positions in the irradiation chamber was determined using the ferrous-ferric dosimeter. A glass vessel containing an oxygen-saturated 0.8N sulfuric acid solution of 10^{-3} M ferrous ammonium sulfate was placed in the copper sample tubes of the irradiation chamber and irradiated. The amount of ferric ion formed was determined by comparing UV absorption at 305 mμ with standard curves made with known ferric ion concentrations. The dosimetry was based on a ferric ion yield of 15.4 μmole/liter/1000 rep.

The dose rate was found to be 7×10^5 rep/hr.

7. Hot Probe for Thermoelectric Power Measurements   The device for measuring thermoelectric power is schematically illustrated in Figure 11. Temperature differentials of up to 300°C can be obtained, limited by the melting or decomposition point of the sample. Normally a pellet on the copper plate at room temperature is contacted by the hot probe of known temperature by means of a screw drive. The temperature difference, ΔT, between the ends of the specimen effects an emf which is measured.

8. Pellet Holder for Resistivity Measurements   The pellet holder for mounting samples for resistivity measurements is illustrated in Figure 12. The glass sleeve permits measurements in vacuum or inert atmospheres and at low and high temperatures, by use of suitable baths or furnaces. Depending on the resistivity of the material, a megohm bridge, useful at resistances up to 10^{11} ohm and a vibrating reed electrometer, useful above 10^{11} ohm, are used. Electrical contacts are made with a silver base paint.

V. CONCLUSIONS

1. Acetylene derivatives are sensitive to radiolysis.

2. Radiation-induced polymerization of acetylene derivatives is a chain process.

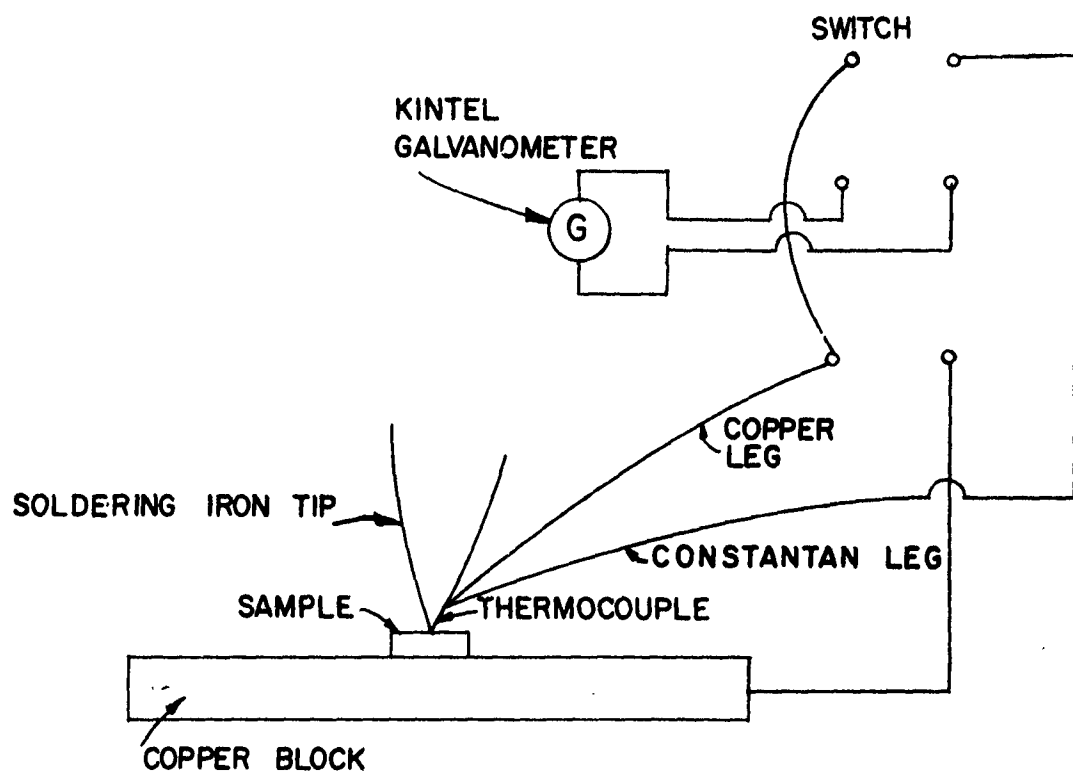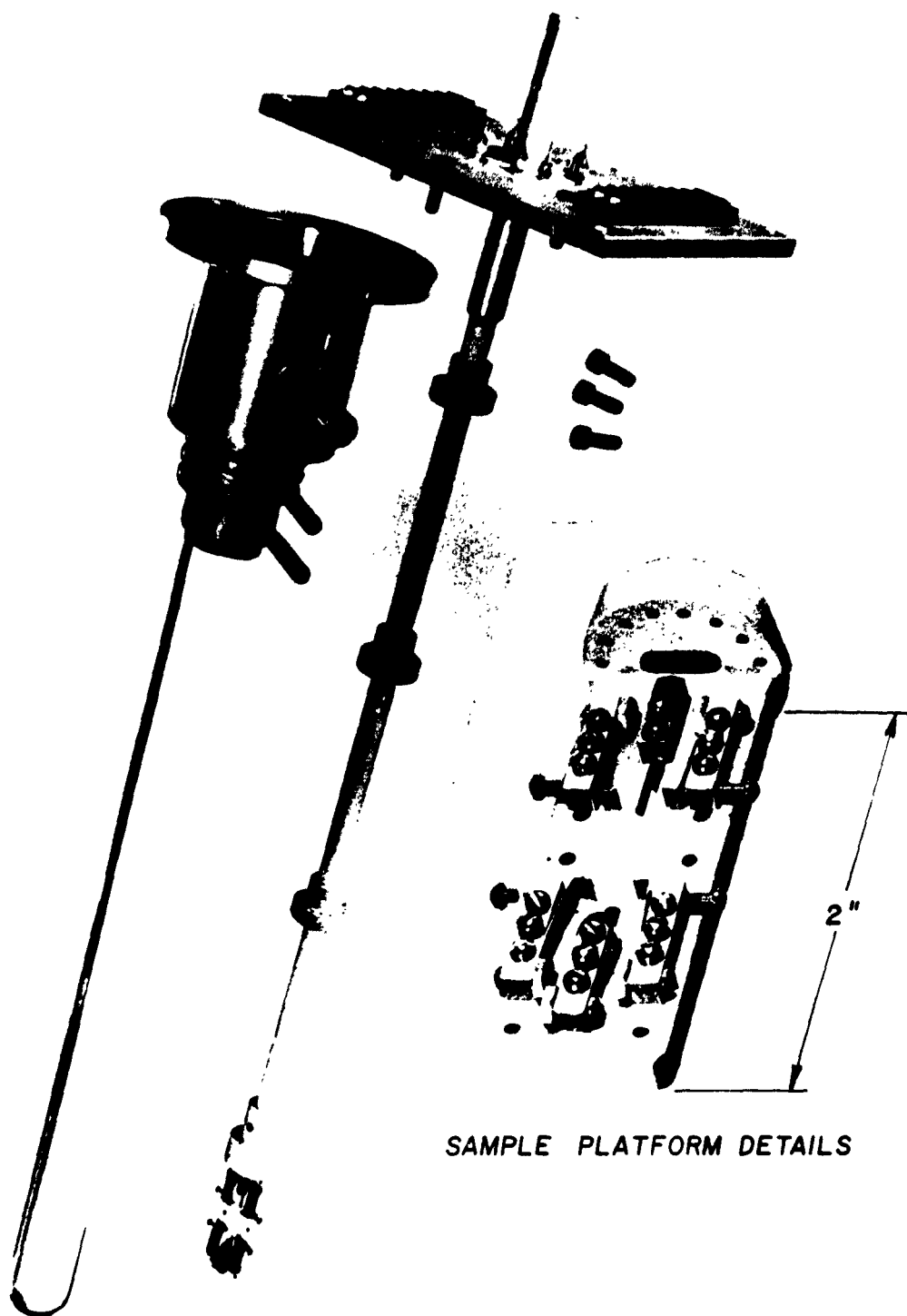3. The most radiation sensitive acetylenic monomers are: propiolic acid, G = 322; neopentylene dipropiolate, G = 177;

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Figure 11.   Hot Probe for Thermoelectric Power Measurements

SAMPLE PLATFORM DETAILS

Figure 12. Pellet Holder for Resistivity Measurements

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pentaerythritol tetrapropiolate, G = 113; and 2-butyn-1,4-dipropiolate, G = 103. Moderately sensitive systems include: phenylbromoacetylene, G = 94; 2-butyn-1,4-diacetate, G = 96; phenylpropiolic acid, G = 73; and bis-(2-hydroxyethoxyethyl)-butyne-2, G = 57.

4. Monomers containing one triple bond give low molecular weight materials and monomers containing more than one triple bond give high molecular weight materials.

5. Among the functional groups, the carboxyl group appears especially sensitive.

6. Temperature, state, dose rate, purity, crystallinity and the use of complexing agents and sensitizers affect the radiation yields but no consistent patterns were observed.

7. Little or no improvement in the electrical properties of the radiation induced polymers over their corresponding monomers was observed.

8. The resistivities of acetylenic monomers are low with respect to organic compounds and similar to values of their respective polymers.

9. Resistivities of acetylene derivative polymers are highly dependent on the physical structure of the solid polymer.

VI. RECOMMENDATIONS

1. Study the radiolysis products from a radiation-sensitive model such as propiolic acid to devise methods for producing high molecular weight polymer. Propiolic acid readily undergoes radiation induced polymerization to low molecular weight materials. Premature chain termination, the chief cause for this low molecular weight formation, may be controlled with a better understanding of the radiolytic by-products and polymerization mechanism.

2. Investigate radiolytic polymers and copolymers of diethynyl aromatics. Monomers containing multiple acetylene groups readily polymerize with radiation to high melting solids. With aromatic groups linking the acetylene functions, highly cross-linked polymers with long uninterrupted conjugation are expected, and would be expected to possess attractive resistivity properties. This area should include diethynyl heterocyclics whose heterocyclic moiety is completely conjugated; e.g., diethynylferrocene. Such diethynyl aromatics

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could be used as comonomers to increase the molecular weight of monoacetylenes which normally form low molecular weight polymers.

3. Prepare and test polyene polymers from phenylacetylene and phenylpropiolic acid derivatives which have electron accepting and donating substituents on the phenyl rings. Based on the work reported above, such molecules are expected to polymerize readily under radiation to solid polymers. By chemical operation on the substituents on the phenyl rings, resistivity and other semiconductor properties can be varied.

4. Select appropriate polymers from (2) and (3) above and investigate the effect of physical structure on polymer resistivity.

5. Prepare, polymerize and define the electrical properties of simple acetylene derivatives containing the following substituents or combinations thereof: $-CN$; $-I$; $-Br$; $-BR_2$; $-CF_3$; and $-MgBr$.

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